GRADIENT ION CHROMATOGRAPHIC DETERMINATION OF RARE EARTH ELEMENTS IN COAL AND FLY ASH

by

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

ABSTRACT

Rare Earth Element (REE) determination in samples of coal and fly ash was undertaken by gradient high performance ion chromatography (HPIC). Ion chromatographic analysis requires that samples be in solution and that the matrix transition metals be removed. Coal samples, weighing 0.20g, were successfully dissolved in sealed pressure vessels in a microwave oven. Standard ashing procedures, followed by acid dissolution, were carried out to allow comparison with the microwave digestion technique. A lithium metaborate/tetraborate fusion and acid dissolution technique was used for the dissolution of fly ash. For the technique of REE determination the sample matrix was removed by off-line cation exchange.

In an initial stage of the HPIC analysis the transition metals were removed by anion exchange using pyridine-2,6 dicarboxylic acid. The REE were then analysed using gradient elution of oxalic and diglycolic acid. Typically a 100µl volume of sample solution was employed for REE determination, but in the case of low ash (low REE) coal samples, prepared by microwave digestion, on-line concentration of 3-5 ml of sample, was necessary. The separated REE were reacted with 4-(2-pyridylazo)-resorcinol (PAR) and detected photometrically using a visible light detector at a wavelength of 520nm.

Reproducibility for each REE was typically better than 5%CoV. Results from the analysis of coal and fly ash international standard reference materials were in acceptable agreement with values from alternative analytical procedures. Smooth, coherent trends obtained when the data were plotted on chondrite and "shale composite" normalised diagrams provided some support for the accuracy of the technique.

The application of HPIC to the determination of REE in coals was demonstrated by the analysis of a new international reference coal sample, USGS CLB-1. Differences in REE concentrations between coal samples prepared by microwave digestion and ashing were observed. The HPIC analytical technique was also applied to the determination of REE in fly ash. The REE concentrations of fly ash from sequential electrostatic precipitators, from Lethabo and Kendal power stations, were determined to elucidate the behaviour of REE after the combustion of coal. REE concentrations increased through the sequential precipitators.

CHAPTER 1

INTRODUCTION

The lithophile elements with atomic numbers of 57 (La) to 71 (Lu) are typically termed lanthanide metals or Rare Earth Elements (REE) (Burt,1989). A major geochemical application of the REE is in the modelling of petrogenetic processes, and the analysis of REE has become an important component of geological studies (Henderson,1984; McKay,1989). Several analytical techniques have been used for the determination of REE (e.g. Inductively Coupled Plasma - Atomic Emission Spectrometry [ICP-AES], Inductively Coupled Plasma-Mass Spectrometry [ICP-MS], Isotope Dilution - Mass Spectrometry [ID-MS] and Instrumental Neutron Activation Analysis [INAA]), but instrumentation is commonly expensive and maintenance costs are high e.g. ICP-MS and ID-MS, or they require access to a nuclear reactor - INAA.

High Performance Ion Chromatography (HPIC) allows for the analysis of a wide range of elements and chemical species in aqueous solutions. Recent developments in HPIC instrumentation, namely microprocessor controlled variation of eluent composition ("gradients") and the introduction of entirely metal-free systems, has extended the scope of the technique to trace metal analysis in geological samples. With detection limits at the part per billion (ppb) level, HPIC has considerable potential for the determination of ultra-trace concentrations of elements. While a wide range of analytical procedures have been developed, few have as yet been adapted and applied to geological samples. However, Ion Chromatography has been applied successfully to the determination of REE in geological matrices, and provides a convenient, low cost alternative to the techniques listed above.

The chemical and physical properties of the individual REE are extremely similar, resulting in similar behaviour. The REE normally exist in the stable 3^+ oxidation state in solutions, and their ionic radii gradually decrease with increasing atomic number (lanthanide contraction). Exceptions in nature are Ce which may occur in the 4^+ state under oxidising conditions, and Eu which can have a 2^+ valency under reducing conditions (Burt,1989), i.e. dominantly 2^+ in

geological environments. The very similar behaviour of the REE prevents separation of the individual elements as trivalent cations. However, an increase in selectivity of the ions may be brought about by using different chelating agents, so separating the REE as cationic or anionic complexes.

REE are routinely determined in igneous silicate rocks by HPIC following anion exchange separation (le Roex & Watkins,1990). The technique allows for the determination of all naturally occurring REE except Ho and Lu. REE data for South African coal and fly ash remain limited, despite extensive research recently undertaken on the chemical composition of South African coal and fly ash (Willis,1987; Bosch,1990). Fly ash is the ash residue of burnt coal, removed from the flue gas at coal burning power stations. The aim of this study was to expand the analytical technique for REE analysis by HPIC to include coal, including low ash (low REE) varieties, and fly ash. REE concentrations of coal were of interest as they provide some indication as to the provenance of coal. The determination of REE in fly ash is of economic significance, as they are concentrated into the fly ash during combustion of coal and may constitute a useable by-product of the ash.

Cation exchange separation of REE may be used as an alternative to the anion process mentioned above. However, in this study problems were encounted in developing this technique for coal analysis as the matrix elements coeluted with the elements of interest.

Like other "wet chemical" analytical techniques samples must be in solution for analysis by gradient HPIC. Extensive experimentation was performed involving acid dissolution, fusion and microwave digestion procedures, to determine the most suitable method of sample preparation for REE analysis of coals and fly ash. The dissolution of coal was achieved by microwave digestion, which removed the necessity of ashing, and was consequently rapid. The risk of contamination was minimised by the use of closed high-purity PTFE (Perfluoroalkoyl Tetrafluoroethylene [Teflon]) pressure vessels. To evaluate the microwave dissolution technique coal samples were also prepared by ashing followed by acid dissolution. Fly ash samples, which frequently contain resistant minerals (e.g. spinel and zircon), were taken into solution after fusing with lithium metaborate/tetraborate (Li-borate). Acid

dissolution and microwave digestion were unsuccessful when applied to the dissolution of fly ash.

Different approaches were required for the analysis of the REE in coal and fly ash, due to their considerable differences in concentration. Fly ash samples mostly contain REE concentrations similar to those of silicate rocks, and therefore were directly injected onto the separator column by means of a sample loop. Similarly, REE determination from sample solutions of ashed coal was possible by direct injection of the sample onto the separator column. Coals prepared by microwave digestion had insufficient REE to allow satisfactory analysis by direct injection. Instead, a procedure of on-line sample concentration was developed, to provide adequate detection limits for the coal samples. Particular care was necessary to ensure satisfactory reproducibility of the concentration procedure.

International Standard Reference Materials were analysed to determine the accuracy of the analytical technique. Results from REE determination of coal and fly ash, using the HPIC techniques, were comparable to published data from other methods and precision was typically less than 6% "coefficient of variation" (CoV). Following the analysis of Standard Reference Materials the technique was applied to the determination of REE in a new reference coal sample, USGS CLB-1.

The procedure for the analysis of REE in fly ash was applied to samples from two South African power stations, to elucidate the behaviour of the REE after combustion. Fly ash from Kendal and Lethabo Power Stations, in the Transvaal, was analysed as both power stations have seven sequential electrostatic precipitator fields, rather than the usual four fields at other stations. The extra three precipitators are designed to cope with the high ash content of the pulverised coal that is burnt. To confirm that the samples supplied were correctly labelled, they were also analysed by X-Ray Fluorescence Spectrometry (XRFS), enabling the measurement of other elements known to vary in concentration sequentially in the precipitators (Bosch,1990). Results indicate a slight increase in REE concentration from the first precipitator field to the seventh.

CHAPTER 2

ION CHROMATOGRAPHY - PRINCIPLES AND INSTRUMENTATION

"Chromatography" denotes a number of separation techniques based on the distribution of solutes between a stationary and mobile phase (Weiss,1986). Ion exchange chromatography can be used for separating inorganic and organic anions and cations. Modern ion chromatography, High Performance Ion Chromatography (HPIC) analysis, enables continuous on-line detection of separated ions. The flexibility of HPIC offers many advantages (speed, sensitivity, selectivity and simultaneous analysis) over other analytical techniques e.g. Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP - AES).

Ion exchange is one of the oldest separation processes described (Weiss,1986). Modern ion exchange chromatography differs from classical column chromatography in three main ways: i) resin composition, ii) the way in which a sample is loaded onto a column and iii) detection is now automated (Small,1990). Classical column chromatography typically uses a column length of 10 - 50cm and diameter 10 - 20mm, and the column is packed with exchange resin of particle diameter 75 - 250 micron e.g. Dowex Resin. After loading a sample onto a classical exchange column, large volumes of eluent (which may be in excess of a litre) separate the ions by flowing through the column under the influence of gravity. This process is applied in the present study in removing matrix elements prior to HPIC analysis (the necessity of this separation process is discussed in Chapter 4). Modern HPIC requires small samples of 50 - 400µl, which allows greater peak resolution so improving the quality of the analyses. Small et al. (1975) did most of the pioneering work on automated detection which enables continuous on-line monitoring of the eluted ions.

2.1 PRINCIPLES OF CHROMATOGRAPHY

The essential principle of ion exchange chromatography is an ion exchange process between a mobile phase and the covalently bound exchange groups of a stationary phase. The aim of

chromatography is to separate the components of a sample into discreet bands, or peaks on a chromatogram, as they move through an exchange column. The process is dynamic as ion species are constantly transferring between phases as well as advancing through the column under the influence of the mobile phase (eluent).

Resins used in ion chromatography have a fixed charge and an associated counter-ion, making the resin electrostatically neutral. During the exchange process the counter-ions are exchanged for sample ions, the latter becoming fixed to the charged resin. The stationary phase determines what separation mechanism is operative, which dictates the eluent composition and often the detection method.

Once a small amount of sample is introduced into the flowing mobile phase, chromatographic sorting onto the stationary phase begins. Due to variations in the affinity of sample ions for the stationary phase, separation of the various sample components is possible (Weiss,1986). Ions of a species with a high affinity for the stationary phase will spend a greater fraction of time on the column than those with a low affinity, thereby effectively separating the two species. Sensitivity decreases and peak broadening increases for ions which elute late (Small,1990; Weiss,1986). Peak broadening is an inevitable feature of chromatography; it is undesirable as it impairs peak separation - resolution. Resolution describes the quality of a chromatographic separation.

A chromatographic peak is rarely perfectly Gaussian, but is typically asymmetric. Two forms of skewing may occur, tailing or fronting (Fig. 2.1). Tailing, which may be ascribed to adsorption processes, is characterised by a rapid increase of the detector signal and a slow decrease. Small (1990) ascribes the process to variations in solute concentration in the mobile phase. The opposite effect is fronting, which is characterised by a gradual rise and rapid decrease in detection signal. Fronting occurs when some sample molecules cannot find free sorption sites on the stationary phase, thus typically indicating column overload. As asymmetric peaks broaden more rapidly than symmetric ones and are less reproducible, skewing is undesirable.

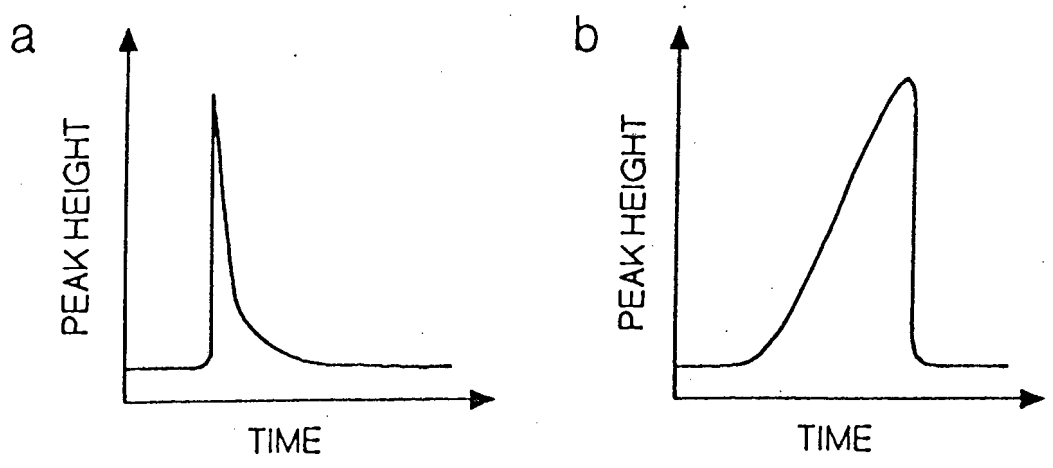


Figure 2.1: The two forms of skewing which may occur;
(a) Tailing, and (b) Fronting.

A greater degree of resolution may be gained by increasing the separation column's length which typically results in an increase in the analysis time and peak broadening. Analysis time and, therefore, peak broadening, may be decreased by varying the strength of the eluent during the analysis - "gradient" elution. Gradient elution is discussed in detail later.

2.2 INSTRUMENTATION

The instrument used in this study was a commercially available 4000i gradient ion chromatograph manufactured by Dionex® Corporation (Sunnyvale, California, U.S.A.). The flow path is made of Polyetherether ketone (PEEK) and is entirely metal free, so avoiding contamination. All instrument components used were manufactured by Dionex®. The REE were separated on Dionex® cation exchange guard and separator columns, and were then detected by a UV/VIS detector. An auxiliary pump was required for on-line concentration. The HPIC laboratory is air conditioned to 20°C, as a stable ambient temperature is preferable for analysis at ultra trace levels.

2.2.1 ELUENT DELIVERY

The instrument comprises four eluent lines which pass via a four-way valve from the eluent bottles through a mixing coil to a dual piston pump (Dionex®,1987). Helium is used to

sparge the eluents, as it has a low solubility in aqueous eluents, to remove dissolved oxygen. Precise flow rate of the eluents entering the ion-exchange column is controlled by a microprocessor, which enables pre-selection, at a set time, of a linear ("isocratic") or gradient flow.

2.2.2 ION EXCHANGE SEPARATION

A sample solution was introduced into the eluent stream via an injection valve which directed the sample onto the separator column (Fig. 2.2). The sample was either drawn into a sample-loop, the volume of which ranged between 50 and 400µl, or alternatively 3 to 10ml of sample solution was concentrated onto a small concentrator column by an auxiliary pump. Slight variations in the plumbing configuration of the injection valve were necessary depending on whether a sample-loop or concentrator column were used (Appendix 1). Two columns could be plumbed into the column select valve at any one time; column selection was made by the control module microprocessor. The plumbing configuration of the column select valve is outlined in Appendix 1. The elements of interest determined the type of separator and guard column and eluents used during separation.

2.2.3 DETECTION

The potential of ion exchange chromatography has been considerably enhanced by the development of suitable detectors (Small, 1990). In this study, following separation, the solutes passed continuously to a UV/VIS detector, that was in-line with the eluent flow.

Eluents were detected photometrically by the UV/VIS detector. An advantage of photometric detection is that it is selective. Detection selectivity may be changed by altering the wavelength monitored or by using various colour forming reagents (Fritz et al.,1982). Throughout this study all elements of interest were complexed with 4-(2-pyridylazo)-resorcinol monosodium (PAR) and detected at a wavelength of 520nm. PAR was delivered at a constant rate of 0.6 - 0.7 ml/min.

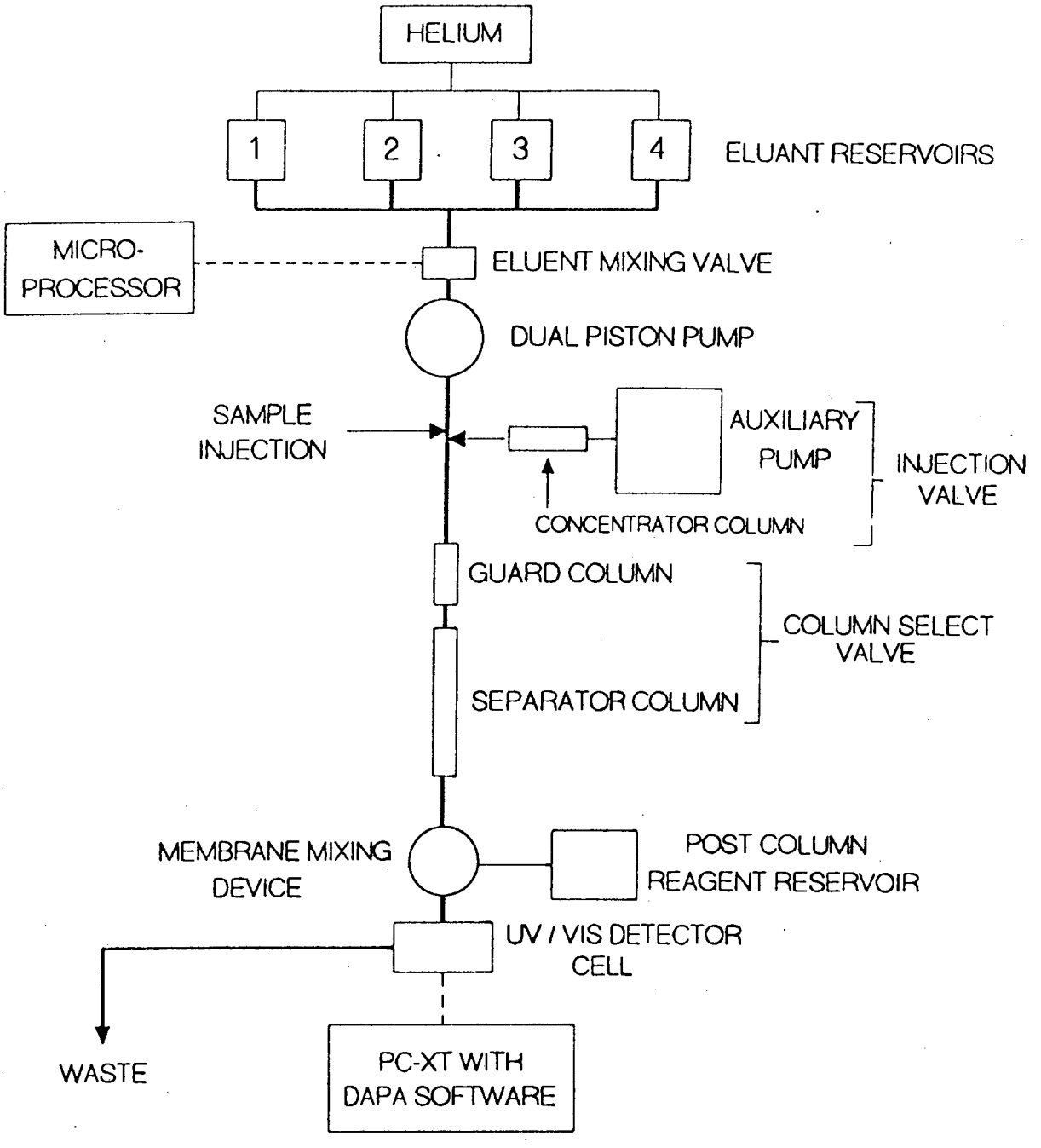


Figure 2.2: Components of the Ion Chromatograph used in this study (DIONEX 4000i).

The PAR solution, the post-column reagent used, is prone to oxidation, resulting in sedimentation. The reagent was prepared in 21 volumes, with 11 being stored in a refrigerator where it was stable for a period of 2 weeks.

2.2.4 DATA PRESENTATION

The resultant chromatogram was recorded on an IBM compatible PC-XT using the commercially available software package DAPA (DAPA Scientific, Kalamunda, Western Australia), which performs peak integration and peak height calculations (le Roex & Watkins,1990).

2.3 ELUENTS

The elements of interest and the column used will determine which eluents are required in any particular separation. Precise selection of eluents, with either linear or gradient flow, is achieved by a microprocessor. Small variations in eluent chemistry can have dramatic results on the chromatogram produced. Consequently great care is required in preparing the eluents in order to minimise disturbances to the chromatograms. While highly accurate weighing of chemicals is unnecessary for satisfactory analysis, it does allow for continuous monitoring of instrument performance. As far as possible only a single eluent was changed on any occasion to facilitate the identification of problems which could arise from variations in eluent composition. The running of a sample blank after any eluent change is a wise precaution to avoid systematic errors.

The water used for making up eluents and samples must be extremely pure, with as low a concentration as possible of trace metals. When rinsing the separator column during the analytical programme the build up of ions on the column from "impure" water may result in their subsequent coelution with the REE elements of interest.

All chemicals used throughout this study were analytical grade. However experience has shown that changing from one brand of chemical to another, of equal specification, can give rise to significant changes in the resulting chromatogram. The importance of eluent purity

was illustrated when separating REE. With continued use of an HPIC CS-5 Dionex® separator column the shape of the Nd peak deteriorated into a "double" peak. The problem was resolved by the use of a highly refined PDCA, manufactured by Dionex Corporation, suggesting that an unidentified contaminant in the various other PDCA brands was responsible. The Nd problem, which bedeviled analyses is discussed in detail in Chapter 5.

CHAPTER 3

SAMPLE DISSOLUTION

High Performance Ion Chromatography, like other wet chemical analytical techniques, requires stable sample solutions. Effective sample preparation methods are important for the reliability of REE determination. A single procedure for the dissolution of solid geological samples cannot be followed because of the diversity of the materials. Several dissolution methods for geological samples have been described by Bock (1979); Jeffery & Hutchison (1983); Thompson & Walsh (1983); Johnson & Maxwell (1989). Three categories of dissolution technique predominate for quantitative dissolution, namely: a) fusion followed by acid dissolution; b) open acid dissolution; and c) microwave digestion using pressurised vessels.

For the determination of REE, complete sample dissolution must be assured, as they frequently occur in considerable concentration in resistant minerals, e.g. monazite, garnet, zircon and some spinels, which are difficult to digest. Several dissolution techniques were investigated in this study, in order to establish suitable procedures for the dissolution of coal and fly ash.

Complete dissolution of coals was achieved by microwave digestion. Coal samples were also ashed to provide data to compare with that from the microwave digestion technique. High temperature lithium metaborate/tetraborate (Li-borate) fusion was successfully used for the dissolution of fly ash. Alternative procedures of $HF/HClO_4$ acid dissolution and microwave digestion were also tried for the dissolution of fly ash. The results and observations of each of the dissolution procedures tried are outlined below. High purity >18 Ohm H_2O from a Millipore Milli-Q water purification system, distilled hydrochloric acid from a sub-boiling quartz glass still, analytical grade reagents and "A-grade" glass-ware were used throughout. Reagent brands used are given in Table 3.1.

Table 3.1: Chemical reagent brands used throughout this study.

REAGENT	CHEMICAL BRAND
HCl	MERCK 37% HCl, distilled to ~6.2M then diluted as required
$HClO_4$	Riedel-de Haën 32% $HClO_4$
HF	Riedel-de Haën 48% HF
HNO_3	Holpro min. 55% concentrated or Riedel-de Haën min. 65% concentrated
H_2O_2	Riedel-de Haën 30% H_2O_2
KHF_2	Riedel-de Haën 99% KHF_2
$LiBO_2$ / $Li_2B_4O_7$	80% Lithium metaborate / 20% Lithium tetraborate, Johnson Matthey Spectoflux 100B

3.1 COAL DISSOLUTION

3.1.1 MICROWAVE DIGESTION

Although microwave ovens have been manufactured for more than 40 years, it is only in the last 15 years that microwave digestion has been used as an alternative to traditional sample digestion methods. The first report on a laboratory application of microwaves appeared in 1974 (Hesek & Wilson,1974), and was followed by a publication (Abu-Samra et al.,1975) concerning microwave sample digestion (Pougnet,1989). Since then the use of microwave ovens for sample preparation has proliferated (Barret et al.,1978; Nadkarni,1984; Fischer,1986; Revesz & Hasty,1987; Matusiewicz & Sturgeon,1989; Pougnet,1989; Nöltner et al.,1990). The initial microwave dissolutions were performed on organic samples. The first published report on microwave digestion of geological samples was in 1983 (Pougnet,1989).

Problems were experienced in early studies with the open vessels used for sample dissolution. as the corrosive fumes damaged the microwave cavity and magnetron. Subsequently, closed pressurized vessels ("digestion bombs") have been employed. Perfluoroalkoyl Tetrafluoroethylene - PTFE (Teflon) has been found to be the most suitable material for these vessels, as it is transparent to microwaves and also extremely pure with very low trace metal concentrations present (Pougnet,1991).

The mechanism by which microwave heating occurs offers several advantages for the chemical decomposition of geological samples. Microwaves eliminate the heat conduction stage of ovens or water baths, as instant uptake of radiation throughout the sample solution causes rapid temperature rise. Intense internal heating and polarization effects may agitate and rupture particle surface layers enabling better contact between acid and sample. Reaction rate and efficiency of acid decomposition generally increases markedly with temperature and complete dissolution may be achieved in a short time (Fischer,1986).

Chemical dissolution processes are further enhanced by pressurized vessels as they allow higher sample - solution temperatures, thereby decreasing the acid to sample ratio required, resulting in lower reagent blanks. Further advantages of closed systems are the avoidance of contamination, both from the environment and cross-contamination between samples, and reduction in the loss of volatile elements. However, it must be borne in mind that since liquid continually absorbs energy during microwave heating, care must be taken not to exceed the digestion vessel's pressure limit as this may lead to vapour leakage and sample loss, or more seriously to rupturing of the vessel (Pougnet,1991).

In this study experimentation was undertaken for the complete dissolution of coal and fly ash. Various parameters such as acid composition (acid mixture), acid to sample ratio, microwave power levels and irradiation times were considered when developing efficient digestion procedures. Development of efficient methods was necessarily based largely upon "trial and error", making development work time consuming.

3.1.2 EQUIPMENT

The equipment used in this study was a MLS 1200 Microwave digestion system manufactured by Milestone GmbH, Leutkirch, Germany. The system was developed for use in the chemical laboratory and comprised a programmable 1200 W microwave module, a heavy duty exhaust module and a microprocessor controlled module for capping and uncapping digestion vessels.

The oven's power settings were programmable in 1% increments from 0% to 50% of power, with further fixed settings at 75% and 100% power. At settings of 25%, 50%, 75% and 100% power the current is continuous. All other settings had pulsating current. The design of the system ensured equal microwave irradiation throughout the oven cavity and included several safety features to guard against explosion and vapour and irradiation leakage.

3.1.3 DISSOLUTION OF COAL BY MICROWAVE DIGESTION

Ashing has typically been required for the dissolution of coal samples in order to remove the large amount of organic component. The procedure is both time consuming and complex. Microwave digestion has been used for a variety of sample types, including organic material (Hartstein et al.,1973; Silberman & Fisher,1979; Nadkarni,1980; Pougnet,1989; Riley & Godbeer,1990), and so was considered a viable option for coal dissolution.

Coal comprises both organic and inorganic material so two stages of dissolution were necessary; one to breakdown the organic material, one to digest the inorganic mineral components. By experimentation, a procedure was developed for the complete dissolution of coal. Parameters were optimised for the simultaneous irradiation of two vessels, each containing 0.1g of sample.

3.1.3.1 *Digestion Vessels*

Teflon medium pressure vessels specially designed by Mr M.A.B. Pougnet (Department of Analytical Chemistry, U.C.T.) were used in this study. These vessels could withstand pressures up to 80 bars. For coal dissolutions the vessels were encased in protective

polypropylene shields and where closed by a hand-held wrench. High pressure is created during the breakdown of the organic components of coal.

Through observations made during experimentation (Appendix 2), it became apparent that the most significant improvements in the dissolution of coal were achieved by increasing microwave irradiation time and power, consequently increasing the internal pressure within the digestion vessels. However, the degree to which irradiation could be increased was limited by the digestion vessels' pressure limits. An increase in the volume of acid used for digestion had only limited effects on the quality of dissolution. The pressure limits of the vessels also influenced the sample size. Coal sample size was restricted by the high pressure created in the vessels as a result of the breakdown of its organic component, necessitating three irradiation steps.

3.1.3.2 *Procedure*

The following 3 step procedure was adopted as the most efficient for coal digestion:

STEP-1: 0.100g of powered sample was weighed into a digestion vessel to which 3ml concentrated HNO_3 were added. The vessel was closed and irradiated for 3 minutes at 25% power and then 4 minutes at 50% power. Two vessels were irradiated simultaneously on a rotating carousel and were then cooled for 15 minutes in a water bath. On opening a vessel, brown NO_2 fumes were sometimes emitted.

STEP-2: 1ml analytical grade 32% H_2O_2 was added to the sample. The irradiation program of Step-1 was repeated. After cooling, the solution appeared green-yellow and the undissolved material grey. The two steps were required to breakdown the organic component of the coal. The resulting solution was evaporated to near dryness by applying 20% power to the open vessels for ~6 minutes, to prevent dilution of the HF used in Step-3. Complete drying was avoided as this gave rise to insoluble residues.

STEP-3: 4ml of 48% HF were added to dissolve the inorganic coal constituents. The two stage irradiation program was repeated.

Two aliquots of each sample were routinely combined after microwave dissolution, to increase the total sample size to 0.2g of coal. 1ml H_2O_2 was added to the combined solution, which

was then evaporated to dryness on a hot plate. The dried, combined sample was dissolved in 10ml 4M HCl and then diluted to 75ml with distilled water. If, on close inspection, no undissolved grains were visible the solution was diluted further to 100ml. When, on occasion, a small amount of resistant inorganic material remained, it was subjected to a "mini-fusion" with potassium hydrogen difluoride (KHF_2), an effective means of decomposition for almost all resistant silicate and oxide minerals (Dolezal et al.,1968).

The mini-fusion involved filtering the incompletely dissolved sample solution through a 70mm diameter Whatman 42 filter paper. The filter paper was then ashed slowly in a Pt crucible over a bunsen burner. 0.25g KHF_2 flux was added to the ash residue. The mixture was gently heated, liberating HF from the flux, after which the temperature was increased to melt the flux and complete the fusion of the resistant undissolved material. The fusion residue, once cool, was dissolved in 1ml $HClO_4$ and evaporated to dryness on a hot plate. A further 0.5ml $HClO_4$ was added and the solution was again taken to dryness before being dissolved in 5ml 4M HCl and diluted to 50ml. The sub-sample was kept separate from the main filtrate.

3.1.3.3 *Sample Size*

REE in coals are contained almost entirely in the inorganic fraction, which comprises 3 - 50% of the coal (Bouška,1981). Within this fraction the REE may be highly concentrated in individual REE-bearing minerals, such as zircon and apatite. Therefore, fine crushing and homogenisation of the coal samples is essential. In order to achieve a representative analysis, as much sample as possible should be used.

In future studies the use of higher pressure digestion vessels in the microwave oven should allow for dissolution of 0.25g sample aliquots (in place of 0.1g), giving a 0.5g sample size when employing the present procedure. The higher pressure vessels will also enable greater degrees of microwave irradiation, either longer time or more power, so reducing the number of irradiation steps required. Milestone have designed a high pressure vessel, the HPV 80, which is capable of withstanding a pressure of 120 bar and temperatures to 300°C (Nöltner et.al,1990). Unfortunately such a vessel was not available for this study.

Despite the small sample size used a high degree of accuracy and precision was obtained during this study, even in the analysis of coals with as little as 10wt% inorganic "ash" content (discussed in Chapter 6).

3.1.4 DISSOLUTION OF COAL FOLLOWING ASHING

During conventional ashing of coal, the volatile and organic component is driven off (Lenahan & Murray-Smith,1986). Care must be taken to avoid loss of particles and volatilization of elements with low boiling points.

3.1.4.1 *Procedure*

Two ashing procedures were evaluated in this study (Table 3.2). In the first the ashing procedure of Bosch (1990) and Lenahan & Murray-Smith (1986) was used. In the second procedure the interval between successive temperature increases was lengthened, i.e. the rate of ashing was slower. For both procedures sufficient coal sample, i.e. 3.00g - 7.00g of pulverised coal, was taken to yield ~0.500g ash after ashing in a muffle furnace. The ashing temperature was gradually increased to prevent smoking and loss of volatile elements, other than carbon and oxygen. After ashing the sample was cooled and weighed, and the percent ash calculated. A Li-borate fusion followed by acid dissolution (discussed later, section 3.2.1.1) was used to dissolve the ash.

3.1.5 COMPARISON OF ASHING AND MICROWAVE DIGESTION FOR REE DETERMINATION

When comparing the two dissolution techniques applied to coal, it is apparent that each has advantages over the other, but both have limitations. The application of microwave digestion is advantageous where a large number of coals are to be analysed on a routine basis, as time saving is considerable and there is little risk of cross-contamination. When only medium pressure vessels are available, the technique is somewhat involved.

Table 3.2: The two ashing procedures used for ashing coal samples.

PROCEDURE 1		PROCEDURE 2	
TEMPERATURE (°C)	TIME	TEMPERATURE (°C)	TIME
110	4 hours	110	1 hour
150	15 min	150	1 hour
250	15 min	250	1 hour
350	15 min	350	1 hour
450	15 min	450	1 hour
500	30 min	500	1 hour
815	30 min	815	1 hour
950	1 hour	950	overnight
1000	overnight	-	-

The ashing procedure is time consuming for routine analysis of coals. Contamination and sample loss are important factors to be considered when ashing. Only two aliquots of a single sample were ashed simultaneously in a muffle furnace in the present study, owing to possible cross-contamination, i.e. transfer of particulate matter between samples. O_2 demand within the furnace is a further limiting factor on the number of samples that could be ashed simultaneously. When REE are to be determined in laboratories where samples are prepared for XRFS analysis using lanthanum-bearing fluxes, such as the UCT Geochemistry Department, it is almost impossible to prevent some degree of REE contamination. In this study, the use of two furnaces and two magnetic stirrers allowed only four sample solutions to be prepared in two days, clearly indicating the time consuming nature of ashing.

A significant advantage of ashing is the large sample size used. 0.500g of ash is fused, then dissolved, representing 3g - 7g of original coal. The greater sample size of ashed samples allows for direct injection of the sample solutions during HPIC analysis, whereas microwave digested samples frequently require on-line sample solution concentration (Chapter 4). A comparison of the REE data obtained from the two dissolution methods will be discussed in Chapter 7.

3.2 FLY ASH DISSOLUTION

3.2.1 LITHIUM BORATE FUSION

Lithium metaborate, sometimes mixed with lithium tetraborate, is a powerful flux which attacks silicate and accessory minerals. Fusion with lithium metaborate/tetraborate has been described by Norrish & Hutton,1969; Boar & Ingram,1970; Cremer & Schlocker,1976; Bodkin,1977; Botto,1981; Crock & Lichte,1982; Thompson & Walsh,1983; Johnson & Maxwell,1989. There are several advantages to the method, notably the relatively low flux to sample ratio of 3 to 1, the fact that almost all minerals are attacked by the flux, and that fusion beads are readily soluble in dilute acids. The method is suited to the preparation of samples for REE analysis, as minerals which are frequently difficult to break down by acid digestion, such as zircon, garnet and ilmenite, are decomposed by the lithium metaborate flux.

3.2.1.1 *Procedure*

The Li-borate fusion procedure of Thompson and Walsh (1983) was followed. The lithium metaborate/tetraborate (80:20) flux (Table 3.1) was weighed into a Pt/Au crucible to which accurately weighed sample was added, and the two were mixed well. Typically a 1:3 sample to flux ratio was used with 0.500g sample and 1.500g flux. The crucible was heated over a bunsen burner at 800°C, until the sample began to melt, then was transferred to a Meker burner at 1000°C and left to fuse for 20 to 30 minutes. The crucible was swirled several times during the fusion to aid mixing. The glass fusion "bead" was left to cool to room temperature then the crucible and "bead" were immersed in a 100ml 0.4M HCl, in a polypropylene beaker (the Li-borate flux solution attacks glass [Thompson & Walsh,1983]). Stirring on a magnetic stirrer with a Teflon-coated stirring bar was begun immediately, in order to dissolve the fusion bead. Within 2 to 3 hours a clear, stable solution was obtained.

3.2.1.2 *Discussion*

Successful dissolution of fly ash samples was achieved using the above fusion/dissolution procedure. Several pertinent observations were made when experimenting with the Li-borate

fusion technique. It was found that dissolution time of the fusion bead was greatly increased, from 2 to 6 hours, when the fusion bead was rapidly quenched. Even after 6 hours of stirring a white precipitate remained. Dissolution time of the fusion bead was also lengthened if magnetic stirring was delayed once the bead was placed in the acid solution, and a white precipitate remained after several hours of stirring. It would appear that an insoluble coating formed around the beads hindering dissolution.

Weak acid was required for dissolution of the fusion bead, as samples precipitated when evaporating a solution with a strong acid matrix. Once precipitation of a sample occurred, it could not be redissolved. Nitric acid may be used for the dissolution of the fusion beads, but for the purpose of this study HCl was more convenient, as dilute HCl solutions were required in the preparation of samples for the analysis of REE, as discussed later. It was difficult to redissolve a sample in HCl that had previously been dissolved in HNO_3 and then evaporated to dryness.

3.2.2 ALTERNATIVE DISSOLUTION PROCEDURES

3.2.2.1 *Hydrofluoric Acid Dissolution*

There are several advantages to using acids, rather than fluxes:- e.g. excess acid can usually be removed by evaporation; acids usually attack fusion vessels less than fluxes because of the lower temperatures employed; and the introduction of large quantities of salts which may be troublesome in later analysis is avoided. Acid dissolution may be performed using oxidising acids (HNO_3, $HClO_4$); non-oxidising acids (HCl, HF) or a combination of both (Crock & Lichte,1982; Johnson & Maxwell,1989).

Hydrofluoric acid dissolution, in combination with other acids ($HClO_4$, HNO_3), is a well established technique for the dissolution of silicate rocks (Thompson & Walsh,1983). As dissolution is usually complete, the procedure is routinely used for the dissolution of samples in which REE are to be analysed. Few minerals remain undissolved under HF attack. Some exceptions are kyanite, zircon, some tourmalines, some spinels, and garnets. Fly ash is

chemically similar to silicate rocks, and therefore the procedure was investigated as a possible alternate to the Li-borate fusion dissolution technique.

Procedure:

The dissolution procedure of Thompson & Walsh (1983), for the analysis of REE, was followed. 1.000 g of finely powered (<250 mesh) sample was weighed into a Teflon beaker, and a few drops of distilled H_2O were added. 6ml of $HClO_4$ and 15ml of HF were added to the digestion vessel, and the sample was left overnight warming on a hot-plate. The solution was evaporated to incipient dryness, then allowed to cool. A further 2ml $HClO_4$ were added to ensure complete removal of all fluoride ions, and the solution was again evaporated to incipient dryness. The sample salts were dissolved in 10ml 4M HCl and transferred to a glass beaker, then diluted to 75ml with distilled H_2O. It was essential to ensure total dissolution of the sample and that the solution was free of cloudy suspension. Frequently heating of the solution over a bunsen burner was necessary to remove cloudiness. If no undissolved grains were present in the sample the solution was diluted to 100 - 120ml. In the event of residual grains, these were subjected to a "mini-fusion", out-lined in section 3.1.3.2 (Dolezal,1968).

Discussion:

The $HF/HClO_4$ dissolution procedure is well tested for the dissolution of silicate rocks for HPIC analysis (le Roex & Watkins,1990). However, problems arose when applying it to the dissolution of several different fly ashes. Using the sample and acid quantities outlined above, only a small fraction of the fly ash was dissolved. No improvements resulted when halving the sample size and maintaining the same acid volume.

The poor dissolution of the fly ash may result from its high component of resistant minerals (relative to silicate rocks) e.g. spinels and apatite, remaining undissolved under HF attack. In addition $HF/HClO_4$ acids may not break-down any residual organic material, remaining from the original coal. Therefore, possibly only the glass, quartz and mullite fraction of the fly ash was dissolved. The TiO_2 content of the fly ashes analysed (determined by XRFS - Bosch,1990) were high relative to silicate rocks, which may have influenced the poor dissolution, as Ti forms insoluble chloride salts (Cotton & Wilkinson,1980). The P_2O_5 content of the fly ashes analysed (~2.5ppm) was also higher than that of silicate rocks. However, it

is not known whether this could have influenced the poor dissolution. Insoluble phosphoric salts may have formed.

3.2.2.2 *Microwave Digestion*

Microwave digestion of fly ash was investigated as an alternate method to Li-borate fusion and acid dissolution. Several combinations of acid, irradiation time and power were tried, to determine the most suitable digestion procedure for fly ash (Appendix 2).

Incomplete dissolution resulted from all tests undertaken for the digestion of fly ash. Further work is necessary before complete dissolution can be achieved. Due to the refractory nature of fly ash it would appear that microwave irradiation time and power play a greater role in its digestion than the volume of acid used. This was apparent from the limited improvements observed in dissolution when increasing the volume of acid utilised during experimentation. Greater pressure would improve the dissolution of fly ash, which would necessitate the use of higher pressure vessels than were routinely available for this study.

CHAPTER 4

SAMPLE TREATMENT

Divalent transition metals behave similarly to REE under the conditions of analysis used in this study. Although the HPIC analytical procedure, used in this study for the determination of REE, allows for the removal of transition metals whose coelution would interfere with the REE chromatogram, the large concentration of transition metals in the dissolved coal and fly ash samples would severely overload the CS-5 separator column. In order to prevent this the bulk of the sample's matrix had to be removed after sample dissolution, prior to injection of the sample onto the separator column. On-line concentration was required for samples with low concentrations of REE, e.g. the low ash coal samples. The procedures required for matrix removal and on-line concentration are discussed.

4.1 BULK REE SEPARATION

The method of matrix separation used was similar to that of Strelow & Jackson (1974), Walsh et al. (1981) and Thompson & Walsh (1983) which have been applied to sample preparation for REE analysis by ICP-AES. Isolation of the REE by cation exchange, as an initial separation stage, is relatively easy due to their similar chemical properties (Korkisch,1989). The REE are strongly absorbed on cation exchange resin from dilute HCl solutions and may be separated as a group, from the sample matrix, by strong HCl. Adsorption is highest from 0.1M to 0.5M HCl, intermediate from 1.0M to 1.75M HCl, and low at higher concentrations, with minimum adsorption occurring from 4M and 8M HCl.

4.1.1 SEPARATION PROCEDURE

The sample, in 0.4M HCl (Chapter 3), was loaded onto a 2 x 19cm column of strong acid cation exchange resin (Spectra/Gel® 100-200 mesh 50X8 H^+ form). Where a "mini-fusion" had been necessary, during sample dissolution, the resulting solution was loaded onto the column before the main sample solution. The matrix elements (transition metals) were eluted

first, with 550ml 1.75M HCl, this solution being discarded. The REE fraction was collected in 550ml 4M HCl. The REE solution was evaporated on a hot-plate to <2ml then made up to a desired volume with distilled water in a volumetric flask. Fly ash samples and ashed coal samples were typically diluted to 20ml, while microwave digested coal samples were diluted to 10ml. The samples were diluted to provide sufficient sample solution for repeated analyses and to enable accurate dilution. On-line concentration of low ash coal sample solutions was required to enable accurate determination of their REE content. Therefore, the 10ml coal sample solution was diluted further to provide sufficient solution for the on-line concentration (section 6.1.1). The final acid concentration of the sample solutions was approximately 0.5M.

Modifications can be made to the above bulk REE separation process, with savings in time and acid quantities used. However, the process was designed for the successful analysis of both coal and fly ash. The great variations in the REE composition of coal and fly ash limited the refinement of the separation procedure.

4.2 ON-LINE SAMPLE CONCENTRATION

The detection limits of HPIC are typically in the ppb range. When employing a 50µl sample loop lower limits of detection are normally 10-100ppb for metals in the sample solution. Although sample injection loops of up to 400µl capacity have been found to work satisfactorily on the 4000i chromatograph, the REE concentrations in low ash coals (1-10ppb) are generally insufficient to enable satisfactory detection by this means of injection.

In order to analyse sample solutions with low concentrations of the REE on-line sample concentration was employed. This technique had formerly been used in the analysis of ultra-trace impurities in waters (Dionex®,1988). It involves the use of an auxiliary pump to pump several *millilitres* of sample solution onto a small "concentrator column", onto which the ions of interest are affixed. This column is then switched into the eluent path, effectively "injecting" the concentrated sample onto the anion separator column.

The technique proved effective in the routine analysis of coals in this study. However, caution is required in this approach since not only are the elements of interest concentrated but the matrix elements are also concentrated, so necessitating very "clean" samples.

4.2.1 OPERATING CONDITIONS

A Dionex DQP-1® auxiliary pump was used to pump the sample solution onto a small "concentration column", a Dionex® CG5 guard column was used for REE analysis. Typically REE from a sample volume of between 3 and 10ml were retained on the concentrator column. The concentrator column was then switched into the eluent path, by means of a 2-way valve switch, effectively transferring the concentrated REE ions onto the separator column. In previous studies, of impurities in water (Dionex®,1988), the sample and standard solutions were pumped onto the concentrator column at a pre-determined flow rate for an accurately measured period of time. This procedure gave poor reproducibility when applied to samples in this study, as explained below. To ensure that the auxiliary pump remains primed, the sample inlet tube should be kept in distilled water, so preventing air intake.

4.2.2 DISCUSSION OF TECHNIQUE

4.2.2.1 *Effects of Acid*

When distilled water was pumped through the CG5 "concentrator column" by the auxiliary pump, using a predetermined flow rate and a pre-set time interval accurately controlled by the HPIC microprocessor, a high degree of reproducibility was measured. However, when concentrating a REE standard solution, in a 0.5M HCl matrix, reproducibility was poor. Flow rate through the column was affected by differing degrees of swelling, caused by the HCl, of the concentrator column resin.

To determine the effects of acid concentration on flow rate, through the concentrator column, two REE standard solutions in 0.2M and 0.5M HCl were prepared. Constant operating conditions were maintained for both standards. The time required to-pass 5ml of each standard was recorded. 3.8 minutes was required for the 0.2M HCl standard and 4.5 minutes

for the 0.5M HCl solution. It was concluded that an increase in acid strength resulted in greater swelling of the concentration column resin. Acid strength did not appear to effect the resulting chromatogram, as integration values for peak height and area remained constant.

4.2.2.2 *Volume Measurements*

Poor results were obtained when using a pre-determined flow rate for concentrating samples. The difficulty was overcome by pumping a suitable volume of sample through the column and measuring the exiting volume by means of a plastic, non-wetting, measuring cylinder.

4.2.2.3 *Accuracy and Precision of the On-line Concentration Procedure*

To determine the accuracy of the on-line concentration procedure, for the analysis of REE, two REE standard solutions were analysed five times in sequence. The REE concentrations in the standard solutions were equivalent to a basaltic rock and North American Shale Composite (NASC) (Appendix 3). 5ml of both standard solutions were concentrated to enable REE determination, by HPIC anion exchange analysis. The basaltic standard was used to determine the REE concentration of the NASC standard. Reproducibility was better than 5%CoV for most elements, with only Tm (9.1%) showing greater relative error (Table 4.1). The percentage difference between the mean and the actual value, for each of the REE, was less than 4 %.

The precision of the on-line concentration procedure was further tested by analysing a single low ash coal standard reference material (SRM), NBS-1632a, five times in sequence. The results show a CoV of better than 4% for most elements, with only Eu (5.6%) and Tm (11.0%) showing greater relative error, probably on account of their low concentration in the sample (Table 4.2).

4.2.2.4 *Preventing Carry-over*

To determine the volume required to remove all traces of a previous analysis, a simple test was performed using Methyl Orange indicator and a weak acid solution. Approximately 1ml

Table 4.1: Accuracy and precision of REE data for a synthetic standard, Std-S against Std-A. after on-line concentration. (n=5)

	Actual (ppm)	$\bar{x}$ (ppm)	sd (ppm)	CoV (%)
La	3.20	3.33	0.083	2.49
Ce	7.30	7.35	0.103	1.40
Pr	0.79	0.80	0.019	2.34
Nd	3.30	3.32	0.056	1.69
Sm	0.57	0.58	0.017	2.86
Eu	0.15	0.15	0.004	2.97
Gd	0.52	0.53	0.009	1.69
Tb	0.09	0.09	0.008	9.13
Dy	0.58	0.59	0.004	0.77
Er	0.34	0.34	0.019	5.68
Yb	0.31	0.30	0.015	4.93

Table 4.2: Reproducibility of the on-line concentration procedure, using coal standard reference material NBS-1632a. REE concentrations in ppm.

	1	2	3	4	5	$\bar{x}$	sd	%CoV
La	12.8	13.0	12.9	12.9	12.9	12.9	0.060	0.47
Ce	26.2	25.9	25.9	26.3	26.3	26.1	0.229	0.88
Pr	3.26	3.21	3.22	3.25	3.30	3.25	0.038	1.17
Nd	11.4	11.2	11.2	11.2	11.2	11.22	0.084	0.75
Sm	2.22	2.07	2.03	2.07	2.05	2.09	0.076	3.37
Eu	0.42	0.43	0.44	0.45	0.49	0.45	0.025	5.62
Gd	1.90	1.84	1.88	1.88	1.94	1.89	0.037	1.96
Tb	0.29	0.29	0.30	0.29	0.28	0.29	0.008	2.75
Dy	1.80	1.72	1.74	1.78	1.79	1.76	0.034	1.93
Er	1.05	1.01	1.00	1.04	1.02	1.02	0.021	2.05
Tm	0.14	0.14	0.18	0.16	0.17	0.16	0.017	10.97
Yb	0.98	0.93	0.96	0.95	0.95	0.95	0.018	1.89

of solution cleared the system, i.e. the dead volume was 1ml. Therefore, prior to each analysis, 2ml of the sample being analysed was pumped through the concentrator pump and valve to prevent carry-over from the previous sample.

4.2.2.5 *Sample Analyses*

Once satisfactory accuracy and precision for the on-line concentration procedure was obtained, the technique was applied to the analysis of coal standard reference materials (Chapter 6).

CHAPTER 5

RARE EARTH ELEMENT DETERMINATION BY GRADIENT ION CHROMATOGRAPHY

The bulk separation of the REE from a sample matrix (Section 4.1), by cation exchange (Strelow & Jackson,1974), was possible due to the very similar chemical behaviour of the REE. The similar chemical properties of the REE normally precludes separation of the individual elements with adequate resolution for quantitative analysis. However, the REE may be separated as individual ions by the use of chelating agents, with the REE being separated as either cationic or anionic complexes. Several processes employing chelating agents have been described for the separation of individual REE (Crock et.al,1984; Heberling et al.,1987; Cassidy,1988; Korkisch,1989; Webster & Gilstrap,1990), with cation exchange being more frequently used than anion exchange. Dionex® (1987) have published techniques for gradient ion chromatographic separation of REE by both anion and cation exchange. During the present study both ion exchange techniques were tested for the determination of REE in coals and fly ash.

5.1 STANDARDISATION

REE concentrations were determined against mixed REE standard solutions prepared from commercially available 1000ppm atomic absorption spectroscopy (AAS) single element standard solutions (Aldrich Chemical Co., Milwaukee) (except Tm [CSIR, Pretoria]). The concentrations of individual elements in the stock solution were equivalent to half those present in a North American Shale Composite (NASC) (Appendix 3, McLennan,1989). Each standard solution was made up in a 0.5M HCl matrix, to match the sample solutions. The sample and stock solutions were diluted to provide closely equivalent REE concentrations. A standard solution was run either after each sample or every second sample. Care was taken to ensure equivalent integration of the peaks for both samples and standards.

In an earlier study of igneous silicate rocks, le Roex and Watkins (1990) prepared calibration plots for each of the REE, to show that there was a straight line calibration curve up to ~8ppm of individual REE in solution (using a 100µl sample loop), at which state the CS-5 column was overloaded. Instrument precision was better than 5% CoV for all REE.

5.2 CATION EXCHANGE SEPARATION OF THE RARE EARTH ELEMENTS

The REE are not easily separated by cation exchange as trivalent cations. However, a number of HPIC methods employing cation separation in the determination of REE have been reported (Henderson,1984; Dionex®,1987; Heberling et al.,1987; Brookins,1989; Jones & Bezuidenhout,1990). An HPIC method in which α-hydroxyisobutyric acid (HIBA) is employed as a chelating agent, forming positively charged complexes with the REE, has been described by Dionex® (1987). In this technique, REE are separated as cation complexes. The REE of heaviest atomic mass, with the smallest ionic radius, forms the least positively charged complex, producing an elution order of Lu to La (Fig.5.1).

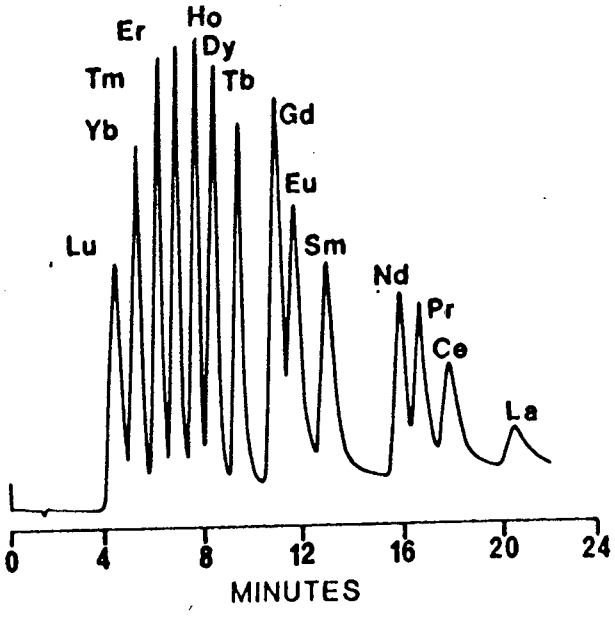


Figure 5.1: Chromatogram produced for a REE standard solution by cation separation, showing the Lu to La elution order (Dionex®,1987).

The elution order of Lu to La is favourable for the analysis of many geological samples, since the least abundant REE are eluted early during the elution sequence when peaks are characteristically sharper and sensitivity is, therefore higher (Fig.5.1). The more abundant light REE are eluted later in the run when sensitivity is reduced by peak broadening. The technique provides good sensitivity in "peak height" for Lu and Tm, which are normally present in very low concentrations (<0.2ppm) in coals and fly ashes.

Although off-line matrix separation was undertaken prior to analysis of the REE, it proved impossible to prepare REE sample solutions entirely free of trace amounts (ppb) of transition metals. The presence of ppb levels of transition metals causes significant interferance on the chromatograms when separating REE as cation complexes. An additional drawback of the cation separation method is the high cost of the HIBA chelating agent, which is considerably greater than the cost of chelating agents used in anion separation.

5.2.1 ION CHROMATOGRAPHIC ANALYSIS

The REE were separated on an HPIC-CS3 separator column with an HPIC-CG3 guard column, during an analytical run of 23 minutes. Separation of the REE is brought about by chelating with a 0.4M solution of HIBA in deionised water, adjusted to pH 4.6 with LiOH. The separation program comprises an 18 minute linear gradient of HIBA and H_2O, followed by 5 minutes of isocratic elution, with a further 10 minutes required for re-equilibration prior to the injection of the next sample solution (Table 5.1) (Dionex®,1987). Following elution, the REE complexes were reacted with the metal complexing agent 4-(2-pyridylazo) resorcinol (PAR) and detected photometrically at a wavelength of 520nm.

5.2.2 DISCUSSION

When analysing REE solutions significant problems were encountered. A drawback of gradient elution is a variation in baseline as eluent composition varies. The baseline rose steeply resulting in poor peak resolution, and severe matrix effects precluded the analysis of REE. Experimentation undertaken to overcome these difficulties is discussed.

Table 5.1: Analytical conditions for the analysis of REE by cation exchange chromatography (Dionex®,1987).

Sample Loop Volume	100µl	
Guard Column	HPIC-CG3	
Separator Column	HPIC-CS3	
Eluent 1	Deionised Water	
Eluent 2	0.4M HIBA	[41.64g/l 2-hydroxyisobutyric acid in deionised water, adjusted to pH 4.6 with LiOH]
Flow Rate	1.0ml/min	
Post-column Reagent	0.2mM PAR	0.10g/l H_2O
	3M NH_4OH	240ml 25% trace metal grade ammonium hydroxide
	1M CH_3CO_2H	57ml trace metal grade glacial acetic acid
Mixing Device	Membrane reactor reaction coil	
Detector Wavelength	520nm	

Gradient Eluent Program:

Time	Eluent 1 (H_2O)	Eluent 2 (HIBA)	Type of elution
0.0	86%	14%	
18.0	30%	70%	Gradient
23.0	30%	70%	Isocratic
23.1	86%	14%	
33.0	86%	14%	Isocratic

5.2.2.1 *Rising Baseline*

Under the conditions outlined in Table 5.1 the REE were eluted on a steeply rising baseline and peak resolution was poor (Fig.5.2). In an attempt to reduce the rise of the baseline, REE standards were analysed at several different absorption level settings (0.02; 0.05 and 0.1AU). No change in the nature of the baseline was apparent at the different settings. At an absorption level of 0.1AU extreme baseline fluctuation swamped the REE peaks. In a final attempt to level the baseline the gradient elution program was changed to an isocratic 100% HIBA elution. The REE were eluted as a single broad peak, with no separation of individual ions. Evidently the rising baseline was associated with the increase in the HIBA gradient. It was concluded that some impurity in the eluent was reacting with the PAR post-column reagent and producing the rising baseline. The eluent brand was changed to a chemical brand of higher purity (from 94% to 99% pure), with no improvement being made to the chromatogram's background.

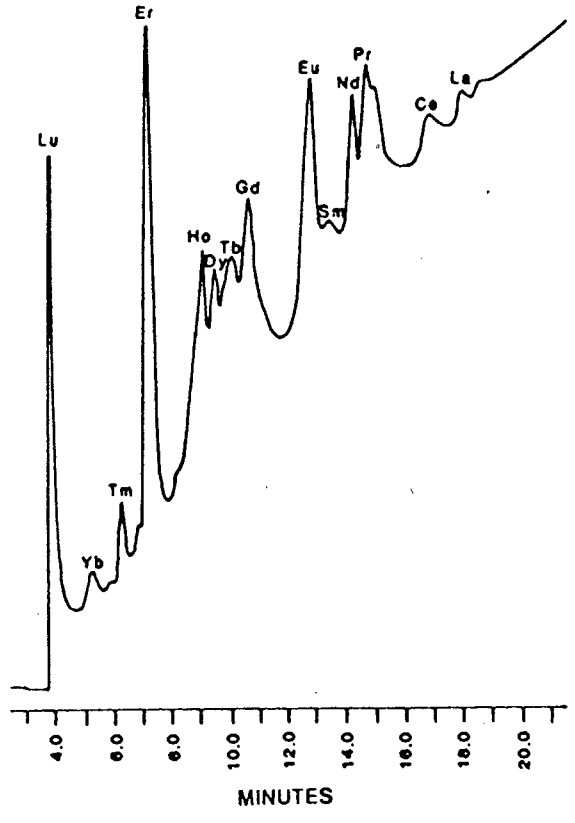


Figure 5.2: REE chromatogram of a standard solution showing a steeply rising baseline and poor peak resolution.

5.2.2.2 *Water Blank*

Reagent blanks were routinely run when a new separation procedure was tested. The running of a H_2O blank was necessary while using the HIBA chelating agent, as several peaks were eluted from standard solutions containing individual REE. Elution peaks were present on the chromatogram of the H_2O blank. Evidently some impurity in the eluent was reacting with the PAR post-column reagent and producing the observed peaks.

5.2.2.3 *Matrix Effects*

A severe limitation of separating lanthanide metals by cation exchange is the coelution of matrix elements with the REE. Experimentation was conducted in an attempt to separate the matrix elements from the REE.

The elution program outlined in section 5.2.1 (Table 5.1) was modified to include an initial HCl wash. Standard solutions containing a limited number of REE and transition metals were analysed using the modified program. 0.1M HCl was run prior to HIBA for 5 then 15 minutes; elution times of the transition metals were unaltered. Approximately 6 minutes after the elution program was reset to HIBA a large intereference peak was observed on the chromatogram. For all HCl strengths tried, a peak occurred 6 minutes after resetting to HIBA. The intereference peak on the chromatogram may have resulted from some impurity present in the HCl acid, despite distilled HCl acid being used, forming an anionic complex, which was only removed from the separation column after 6 minutes of HIBA elution.

When increasing the HCl strength to 0.4M, Fe and Zn were eluted during the acid wash. However, Er was eluted at the same time as the HCl interference peak. The duration of the HCl wash did not influence the resolution of the REE peaks. The REE were eluted during the acid wash when concentrations of 0.75M and 1.0M HCl were used.

A 4 minute H_2O rinse was included between the HCl and HIBA eluents, in an attempt to eliminate the HCl interference peak. No improvements were observed; instead the chromatogram was further complicated by the presence of a water dip. The HCl interference

peak continued to occur 6 minutes after resetting the elution programme to HIBA. There was no improvement in the resolution between individual REE, as the REE and transition metals eluted during the H_2O wash. The cation exchange separation technique was therefore, eliminated as a feasible method for the determination of REE in geological samples.

5.3 ANION EXCHANGE SEPARATION OF THE RARE EARTH ELEMENTS

Strong complexing agents, such as oxalic and diglycolic acid, may be used to form lanthanide metal anionic complexes which can be separated by anion exchange (Dionex®,1987; Herberling et al.,1987). The best separation for the individual REE is achieved using opposing linear gradients of oxalic and diglycolic acid. The strongest complexes (the smallest ions i.e. the REE of highest atomic number) are the most negatively charged, and are eluted last, resulting in the elution order being reversed from that of cation exchange separation (Dionex®,1987). Hence the elution order is La to Lu (Fig.5.3).

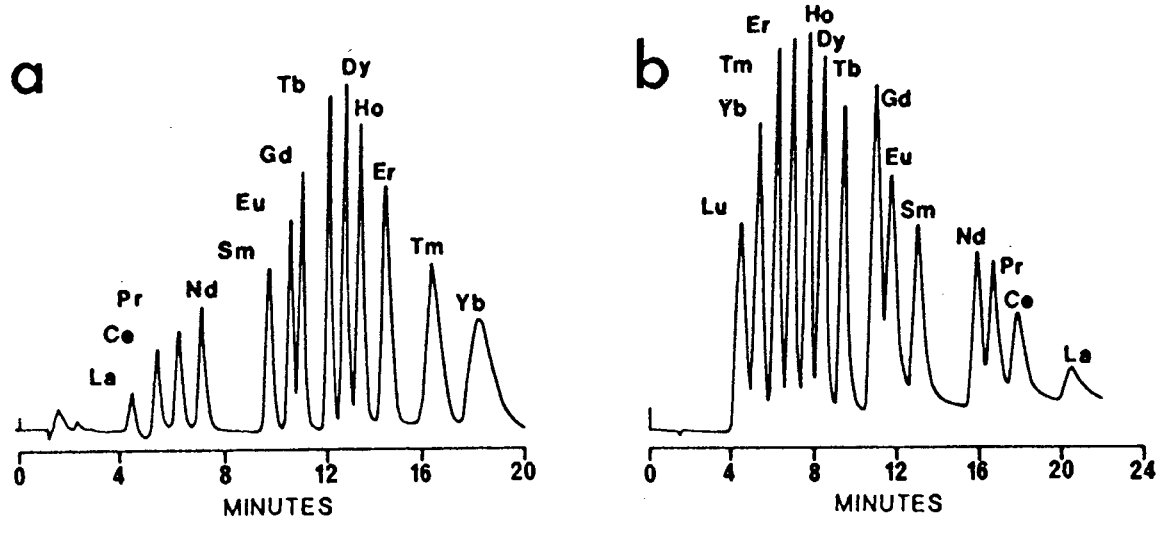


Figure 5.3: Chromatograms produced for solutions containing equal concentrations of each REE by (a) anion separation and (b) cation separation, showing relative sensitivity for each element when reacted with PAR (Taken from Dionex®,1987).

As mentioned previously, it proved impossible to prepare REE sample solutions completely devoid of trace (ppb) levels of transition metals. Coelution of these metals with the REE causes problems which may be overcome using an initial elution with pyridine-2,6-dicarboxylic acid (PDCA). Separation of the transition metals from the REE is achieved using the differences in their electro-selectivity. The transition metals form monovalent or divalent anionic complexes with PDCA, whereas the REE form trivalent complexes with PDCA. The transition metals are removed from the separator column with PDCA, while the REE are strongly retained on the column (Fig.5.4). The lanthanide metals are removed from the column with oxalic and diglycolic acids. The complete removal of the transition metals ensures a REE chromatogram free of matrix interferences. The ability to effect complete separation of the transition metals from the REE by anion separation is a critical advantage of the anion over the cation separation technique.

5.3.1 ION CHROMATOGRAPHIC ANALYSIS

Separation of the REE was performed on an HPIC-CS5 separator column with an HPIC-CG5 guard column. The analytical program for the elution of REE comprised an initial 12 minutes of PDCA elution, to wash off the transition metals; a 5 minute wash with distilled water was necessary between the PDCA and oxalic/diglycolic acid elutions; a 4 minute isocratic elution of oxalic acid and H_2O followed. Separation and removal of the REE from the separator column was effected by a 9 minute linear gradient elution of H_2O, oxalic and diglycolic acid, followed by a 14 minute isocratic elution of the final gradient settings (Fig.5.4). A single analytical run took 44 minutes with a further 16 minutes required for re-equilibration prior to injection of the next sample. Full analytical conditions are given in Table 5.2. After elution, the REE complexes were reacted with PAR, then detected photometrically at a wavelength of 520nm.

5.3.2 DISCUSSION OF TECHNIQUE

The extreme flexibility of HPIC analysis enables subtle modifications to the quality of REE chromatograms to be made by changing various parameters. A discussion of the influences

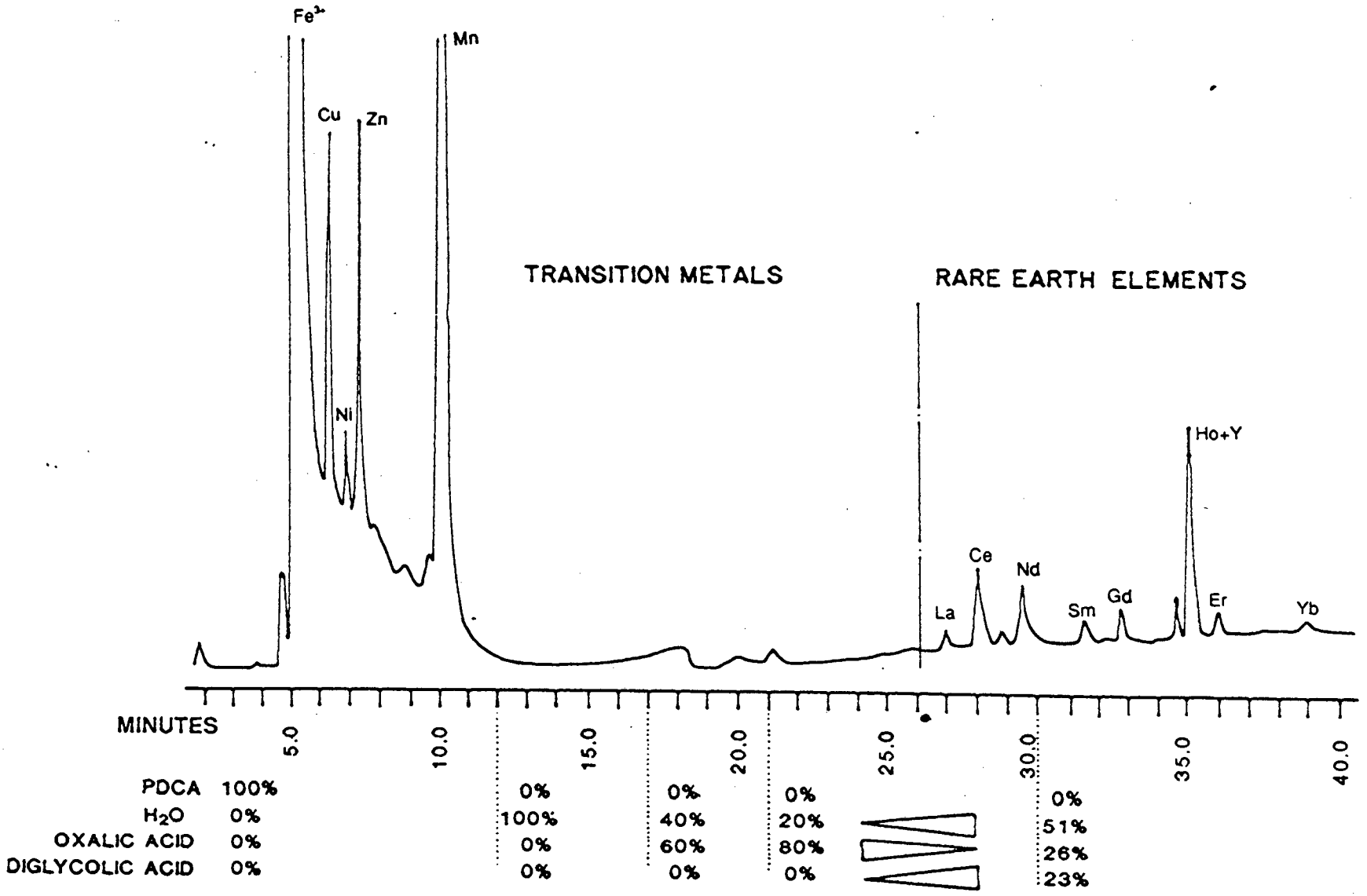


Figure 5.4: Entire chromatogram for an analysis of a sample of USGS CLB-1, showing complete separation of the transition metals from the REE. The elution programme is also shown.

Table 5.2: Analytical conditions for the analysis of REE by anion exchange chromatography (Dionex®,1987).

Sample Loop Volume	100µl	
Pre-concentrator Column Volume	Typically 5ml	
Guard Column	HPIC-CG5	
Separator Column	HPIC-CS5	
Eluent 1	Deionised Water	
Eluent 2	6mM PDCA	1.0g/l Pyridine-2,6dicarboxylic acid
	50mM CH_3CO_2Na	6.8g/l sodium acetate, trihydrate
	50mM CH_3CO_2H	2.85ml/l glacial acetic acid
Eluent 3	100mM Oxalic acid	12.61g/l oxalic acid dihydrate
	190mM LiOH	8.14g/l lithium hydroxide, monohydrate
Eluent 4	100mM Diglycolic acid	13.41g/l diglycolic acid
	190mM LiOH	8.14g/l lithium hydroxide, monohydrate
Flow Rate	1ml/min	
Post-column Reagent	0.2mM PAR	0.10g/l H_2O
	3M NH_4OH	240ml 25% trace metal grade ammonium hydroxide
	1M CH_3CO_2H	57ml trace metal grade glacial acetic acid
Reagent Flow Rate	0.7ml/min	
Mixing Device	Membrane reactor reaction coil	
Detector Wavelength	520nm	

Gradient Eluent Program:

Time (min)	H_2O	PDCA	Oxalic	Diglycolic	Type of elution
0.0	0	100	0	0	
12.0	0	100	0	0	Isocratic
12.1	100	0	0	0	
17.0	100	0	0	0	Isocratic
17.1	40	0	60	0	
21.0	40	0	60	0	Isocratic
21.1	20	0	80	0	
30.0	51	0	26	23	Gradient
44.0	51	0	26	23	Isocratic
44.1	0	100	0	0	
60.0	0	100	0	0	Isocratic

of some parameters on the REE chromatograms follows. Accuracy, precision and detection limits of the technique will be discussed in the following chapter.

5.3.2.1 *Differences in the Order of Anion and Cation Elution*

Gradient elution anion separation enables the routine analysis of all naturally occurring REE except Ho and Lu, in geological samples. Ho cannot be determined since it coelutes with the more abundant Y. The Lu peak is inadequately resolved from Yb. However, the small Lu peak follows the larger Yb peak and does not contribute to its height, as measured from the chromatograms (Fig.5.5). An advantage of the cation separation order, Lu - La, is the ability to readily determine Lu, since its peak is fully resolved from Yb. Similarly the sharper peaks associated with early elution provide good sensitivity for Tm, the second least abundant REE, during cation separation. Tm is frequently not recorded by anion separation, since it may occur close to or below detection limits, so increasing associated errors when normalised to chondrite values.

Eu is a critical element in geochemical studies as it is the only REE that can occur in the divalent state in igneous systems, and it is fractionated differently from neighbouring Sm and Gd. The magnitude and direction of relative Eu differences, result in Eu anomalies on a chondrite normalised diagram, which may show enrichment or depletion. Eu anomalies can be strongly diagnostic of petrogenetic processes (McKay,1989). The abundance of Eu in rocks is normally lower than that of the adjacent REE, Gd. The Eu and Gd peaks lie in the middle portion of a REE chromatogram and are closely spaced. Modification of the elution gradient does not effect greater separation. The Eu and Gd peaks can be fully resolved when Eu elutes prior to Gd as in the case of anion separation (Fig.5.5). During cation separation significant tailing of the large Gd peak onto the small Eu peak can be expected, precluding the accurate measurement of the Eu peak. During anion separation the Sm peak is adequately resolved from the Eu peak (Fig.5.5).

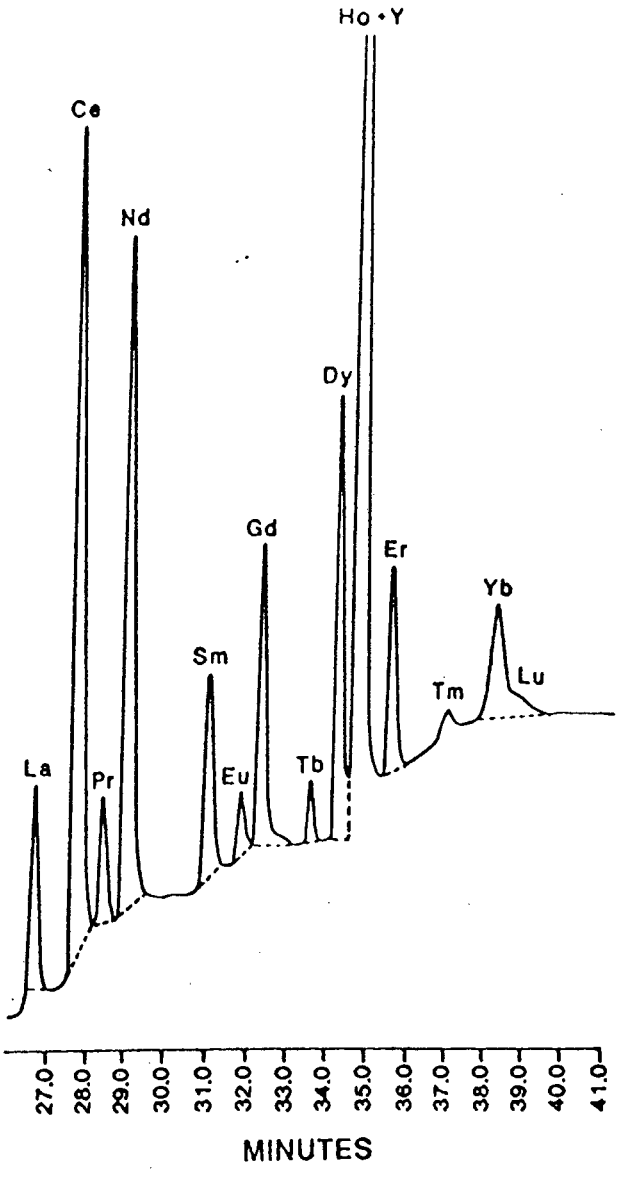


Figure 5.5: REE chromatogram from analysis of a sample of USGS CLB-1. "Peak height" was recorded along a vertical line from peak apex to the selected baseline (dashed line). Note the inadequate resolution of Lu, and the rise in baseline which results from the use of an eluent gradient.

5.3.2.2 *Eluent Chemistry*

As discussed earlier (Chapter 2) precise eluent chemistry is vital for accurate element determination. The chemical behaviour within REE analyses can be complex, and small variations in eluent composition can have profound results on the chromatogram produced. Consequently considerable care is required in the preparation of eluents and high purity chemicals are a necessity. The dangers of minor variations in eluent chemistry are well illustrated by a problem of Nd determination that affected REE analyses throughout much of this study.

5.3.2.3 *The Nd Double Peak Problem*

Deterioration of the shape of the Nd peak was observed after the CS-5 separator column had been used for a number of analyses. A sharp Nd peak (Fig.5.5), with slight positive tailing as seen for all REE peaks, would broaden at the base. In subsequent REE analyses, the broadened base would develop into a definite shoulder and eventually into a second, poorly resolved peak (Fig.5.6). The height of the second Nd peak increased at the expense of the first, resulting in Nd becoming unquantifiable. The first Nd peak tails onto the second, so compromising the possibility of obtaining a Nd value by summing the two peak heights or areas. The development of the second peak was unpredictable, but did not affect the determination of other REE peaks. Determination of the Nd peak was possible when a new or little used column was employed. The appearance of a double peak necessitated the frequent replacement of separator columns, greatly increasing the cost of analyses.

Analysis of all types of geological samples caused degeneration of the Nd peak. However, deterioration was particularly pronounced when analysing coal samples. The Nd peaks of coal samples themselves were single, but the subsequently analysed standard solutions had double Nd peaks. This may indicate that possible matrix elements, from the coal samples, were remaining on the separator column after the analyses and were only being removed during subsequent standard runs. To test this hypothesis a single coal sample was run a number of times in succession. The first analysis had a single Nd peak, while the Nd peak of the second analysis was double. With continued use of the separator column the double peak of the standard solutions worsened and the Nd peaks of coal samples gradually split. To ascertain possible causes of, and ways to overcome, the Nd double peak problem, further experimentation was carried out. The observations noted are discussed.

No interference was visible when a blank was analysed. The Nd peak split even when a standard solution containing only Nd was analysed. This showed that the second Nd peak was not due to the presence of other REE (e.g. dual elution of Ce was suspected as a possibility as Ce may occur in two oxidation states). The Nd value was always low when determined from a double peak, indicating that two Nd complexes were forming. Analytical conditions appeared to cause the Nd peak to split. Optimal sample acidity was found to be

~0.5M. Na_2SO_4 is typically used to rinse columns after storage. Washing the separator column with Na_2SO_4 did not reduce column degeneration. Changing the eluent brands of oxalic and diglycolic acids, i.e. the eluents used to remove the REE from the separator column, had no effect on the appearance of the Nd peak.

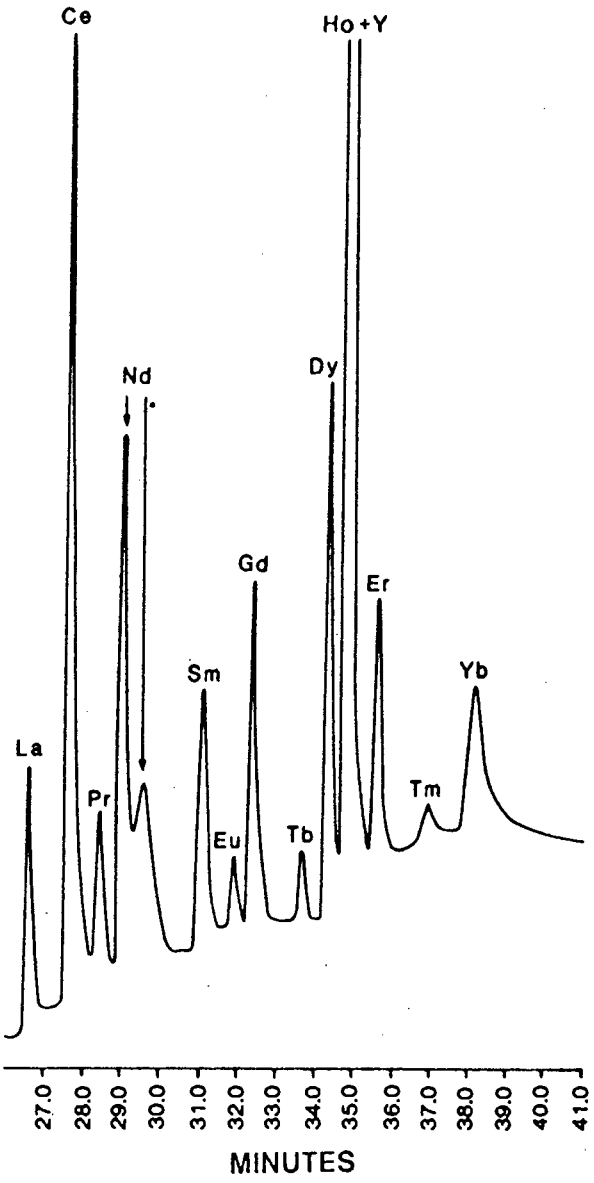


Figure 5.6: Inferior REE chromatogram of a sample of USGS CLB-1 showing the spliting of the Nd peak resulting from an impurity in the PDCA eluent.

It was observed that washing PDCA through the separator column hastened column deterioration, suggesting PDCA was at fault. Therefore, re-equilibration between oxalic acid and PDCA was kept to a minimum. When PDCA was eliminated from the analysis of a

mixed REE standard solution no splitting of the Nd peak occured. The PDCA eluent typically contains 50mM glacial acetic acid. By omitting the glacial acetic acid the deterioration of the Nd peak was delayed. Purification of the PDCA chemicals, prior to eluent preparation, did not improve the shape of the Nd peak. The problem was finally resolved by using highly refined PDCA, manufactured by Dionex Corporation, suggesting that an unidentified contaminant in the various other PDCA brands used, which was not removed during purification, was responsible. It would appear that some impurity in the PDCA aided the formation of a second Nd complex, producing the second Nd peak at the expense of the first. The cost of the Dionex® PDCA is higher than locally available brands, but its use overcomes the expenses incurred by the high cost of frequent separator column replacements.

5.3.2.4 *Gradient Elution*

Adequate resolution of the REE peaks was achieved by the ability of the DIONEX 4000i instrument to run gradients involving up to 4 eluents. Similar resolution using the chemistry of this technique was not possible by isocratic elution. The quality of a chromatogram may be greatly affected by minor changes to the gradient programme. Frequently a balance between resolution and peak width/sensitivity has to be reached, as improvements in one part of a chromatogram may give poorer results elsewhere in the chromatogram. For routine analysis compromise programmes giving satisfactory peak resolution for a range of compositions were required.

Two gradient programmes were routinely used for the analysis of coals and fly ashes. The programmes differed only slightly in the proportions of opposing oxalic/diglycolic acid used to separate the REE. The second programme caused a shortening of the chromatogram and was employed only when concentrations of the heavy REE were low, as only the last part of the chromatogram was affected. The sensitivity (peak height) of Er, Tm and Yb was increased by narrowing their peaks. The programme was unsuitable when the heavy REE were more abundant, as condensing the chromatogram resulted in tailing of the larger Er peak onto that of Tm. Condensing the chromatogram also caused steepening of the baseline's slope which made accurate peak height measurements more difficult.

Although gradient elution is essential to the separation of REE, it does increase the complexity of the analytical chemistry. An effect of this was the fluctuation of the chromatogram's baseline, which usually does not create a problem in REE determination, but necessitates specific procedures of peak measurement. Subsequent to this work it has been found that the geometry of the baseline is influenced strongly by the brands of eluents used. The chemical brands used throughout this study were Aldrich or Reidel-de Haën, which produce a noisy baseline. A flatter baseline has been obtained with the use of Fluka chemicals. Experience has shown that results remain good as long as the peaks are measured carefully.

5.3.2.5 *Detection Sensitivity*

The relative sensitivity of UV/VIS detection at a wavelength of 520nm for each REE following complexing with PAR is illustrated in Fig.5.3. Sensitivity is lowest for the light REE (La-Sm), which are abundant in geological samples. Tb, typically of low abundance, occurs in the region of maximum sensitivity and for the heaviest REE (Er-Lu) sensitivity is intermediate. When varying the detection wavelength changes in the sensitivity for individual REE occur.

Composition of the post-column colouring reagent significantly affects detection sensitivity. An alternate colouring reagent for REE analysis is Arsenazo III (Fritz et al.,1982). This reagent is more specific to REE detection than PAR, but decomposes rapidly (Bezuidenhout, MINTEK, *pers.comm.*). Therefore, the greater stability of PAR makes it a more suitable colouring reagent for routine REE analysis.

5.3.2.6 *Peak Evaluation*

Isocratic elution typically results in well resolved peaks on a flat baseline, enabling automatic integration with suitable software. "Peak area" is typically used in determining ion concentration, with the peaks being defined by the inflection points from the baseline. However, the rising baselines of REE chromatograms present problems with this approach. "Peak height" measurements provide more consistent and reliable results. The DAPA

software package, used in processing the REE chromatograms, permitted the setting up of programmes to delineate individual REE peaks in specific ways. However, each chromatogram had to be checked for correct delineation of peaks, as small variations in the retention times of individual elements caused slight differences in peak delineation. Therefore, routine analyses, but not automatic analyses were possible.

Most of the REE peaks are sufficiently resolved to allow the use of baselines drawn from start to end of peaks - "valley to valley" (Fig.5.5). The large peak given by Y and Ho coelution necessitates that the baseline of the preceding peak, Dy, be specifically defined from the front edge of the peak - "fixed baseline". A similar procedure may be required for the Eu peak. Consistent delineation of the Yb peak must be ensured owing to the following unresolved Lu peak. Consideration of chromatographic peak shapes is required when formulating a programme to delineate peaks, with use being made of the fact that peaks "tail" only onto following peaks, not onto preceding peaks.

CHAPTER 6

REE ANALYSIS OF COAL STANDARD REFERENCE MATERIALS

The accuracy and precision of the HPIC anion separation method, described in the previous chapter, was ascertained by the repeated analysis of international Standard Reference Material (SRM) coal samples. The technique was then applied in the determination of the REE content of USGS CLB-1, of the United States Geological Survey (Watkins et al.,*in press*.).

Analytical results of REE determinations by HPIC in this study generally compare closely with those produced by Instrumental Neutron Activation Analysis (INAA) (Willis & Hart,1985) and fall within the ranges of published values. The HPIC data resulted in highly coherent chondrite-normalised REE patterns. Generally undifferentiated patterns were obtained when the measured REE concentrations were normalised to the North American Shale Composite (NASC), so providing some further indication of the accuracy of the data produced by the technique.

6.1 REFERENCE MATERIALS

Four international SRMs samples were analysed, NBS-1632a, SARM-18, SARM-19 and SARM-20. REE in coals are mostly contained in the inorganic fraction, which comprises 3-50% of the coal (Bouška,1981). The coals analysed during the present study covered a wide range in ash content, from 9.89% (SARM-18) to 35.34% (SARM-20) (Ring & Hansen,1984). Similarly, the total REE abundances recorded in the SRMs were widely different.

6.1.1 SAMPLE PREPARATION AND HPIC ANALYSIS

Five sample solutions from each of the low ash coals, NBS-1632a and SARM-18, were prepared separately by microwave digestion. Single microwave digestion samples were prepared for the high ash coals, SARM-19 and SARM-20. Each preparation was analysed in duplicate. Only on the rare occasion that the duplication was worse than 10% CoV,

indicating a malfunction in the analytical procedure, was a third analysis undertaken. The REE concentrations were determined against a mixed REE standard solution that was run after each sample analysis, in the case of NBS-1632a and SARM-18, or after every second sample. If the reliability of a sample solution or sample analysis was doubted the sample was discarded and the results were not included in this study.

REE determination of silicate rock samples is commonly possible by direct injection of the sample solution onto the separator column via a sample loop of 100µl. Similarly, solutions prepared from high ash coals, such as SARM-20, can be injected directly onto the separator column. However, low ash coal sample solutions, prepared for analysis by microwave digestion, have insufficient REE to allow satisfactory analysis by direct injection when using the maximum practical loop size of 400µl. On-line sample concentration was employed, using the measurement procedure outlined in Chapter 4, to analyse low ash, low REE coals. 5ml of sample were concentrated for each analysis. Since the sample concentration could be performed while the system was re-equilibrating after the previous analysis, there was no addition to the analysis time, despite the extra concentration step.

An acid blank was prepared by the microwave dissolution procedure used for the preparation of coal samples. The blank was analysed for REE, following on-line concentration. The chromatogram was devoid of peaks, indicating the absence of any REE in the reagents used.

6.1.2 DATA

The following data are presented:

1. REE concentrations for NBS-1632a and SARM-18, by HPIC analysis of individual sample solutions prepared by microwave digestion - Tables 6.1 and 6.3.

2. Mean REE concentrations for NBS-1632a and SARM-18 by HPIC, compared to results from published data and INAA values - Tables 6.2 and 6.4.

3. REE concentrations for SARM-19 and SARM-20 by HPIC after microwave digestion, compared to results from published data - Tables 6.5 and 6.6.

4. Chondrite and NASC normalised plots of NBS-1632a, SARM-18, SARM-19 and SARM-20 from HPIC data, compared to plots from published data - Figures 6.1 to 6.4.

6.1.3 RESULTS

6.1.3.1 *Precision*

In an earlier study on igneous silicate rocks, le Roex and Watkins (1990) found instrument precision to be better than 5%CoV for all REE (Tm was not reported). Greater sources of imprecision in the analytical technique applied to coals and fly ashes are liable to originate from (i) the different methods of sample preparation, and (ii) in the case of the low ash coals, use of the novel means of on-line sample concentration.

The reproducibility associated with the entire procedure of coal analysis is indicated by the standard deviation and CoV of results from the multiple analysis of the low ash coals in Tables 6.2 and 6.4. Precision for each element was generally <5% CoV, in spite of the 0.2g sample size. Poorer precision was typically obtained for Tm, since the concentration of this element was close to the lower limit of detection under the conditions of analysis. The small Tm peak was measured by "peak area". Enhanced reproducibility for Tm can readily be achieved by greater on-line sample concentration. This, however, was not routinely undertaken in this study, as it would have rapidly exhausted sample solution, so preventing the repeated analysis of each sample.

6.1.3.2 *Limits of Detection*

Lower limits of detection are difficult to define in view of the number of parameters that can be varied to increase the effective concentration of REE loaded onto the separator column. Detection limits vary according to the size of sample loop and the degree of sample

Table 6.1: REE concentrations (in ppm) for sample solutions of NBS-1632a by HPIC analysis.

	1	2	3
La	12.3	12.9	12.1
Ce	25.5	26.1	25.6
Pr	3.13	3.25	3.16
Nd	11.2	11.2	10.7
Sm	2.28	2.09	2.27
Eu	0.45	0.45	0.47
Gd	1.93	1.89	1.95
Tb	0.28	0.29	0.30
Dy	1.76	1.76	1.76
Er	0.98	1.02	1.01
Tm	0.17	0.17	0.15
Yb	0.94	0.95	0.94

Table 6.2: REE concentrations (in ppm) for NBS-1632a by HPIC analysis (n=3), compared to results from INAA (Willis & Hart,1985) and published data (Gladney et al.,1984).

	HPIC			INAA	PUBLISHED DATA	
	$\bar{x}$	sd	%CoV		$\bar{x}$	Range
La	12.4	0.40	3.19	15	15	10.9 - 19
Ce	25.7	0.22	0.85	31	29	25.7 - 32
Pr	3.17	0.05	1.55	2.9	3.2	3.0 - 3.3
Nd	11.0	0.30	2.73	14	11.4	10 - 15.6
Sm	2.21	0.11	4.98	2.6	2.4	1.1 - 2.8
Eu	0.46	0.01	3.10	0.51	0.53	0.46 - 0.55
Gd	1.92	0.04	1.98	-	2.4	1.9 - 3.0
Tb	0.29	0.01	2.98	0.35	0.31	0.29 - 0.33
Dy	1.76	0.01	0.40	1.9	2.1	1.83 - 2.56
Er	1.00	0.02	1.76	1.1	0.91	-
Tm	0.16	0.01	4.43	-	0.40	-
Yb	0.94	0.002	0.25	1.1	1.03	0.9 - 1.2

Table 6.3: REE concentrations (in ppm) for sample solutions of SARM-18 by HPIC analysis.

	1	2	3	4
La	8.95	8.45	8.89	8.89
Ce	18.8	18.8	19.5	19.2
Pr	2.35	2.27	2.35	2.32
Nd	8.55	8.35	8.52	8.55
Sm	1.69	1.60	1.49	1.67
Eu	0.30	0.31	0.30	0.31
Gd	1.57	1.53	1.52	1.60
Tb	0.27	0.26	0.27	0.27
Dy	1.76	1.69	1.74	1.75
Er	1.16	1.14	1.12	1.17
Tm	0.19	0.18	0.12	0.19
Yb	1.12	1.07	1.11	1.11

Table 6.4: REE concentrations (in ppm) by HPIC analysis of SARM-18 (n=4), compared to INAA (Willis & Hart,1985) and published data (Ring & Hansen,1984).

	HPIC			INAA	PUBLISHED DATA	
	$\bar{x}$	sd	%CoV		$\bar{x}$	Range
La	8.79	0.23	2.64	9.2	10	9 - 16
Ce	19.08	0.32	1.66	21.8	22	12 - 24
Pr	2.32	0.04	1.75	2.6	-	-
Nd	8.49	0.10	1.15	11	-	-
Sm	1.61	0.09	5.51	1.9	2	1.8 - 2.2
Eu	0.31	0.004	1.21	0.31	(0.3)	0.29 - 0.41
Gd	1.55	0.04	2.33	2.0	-	-
Tb	0.26	0.004	1.36	0.32	(0.3)	0.19 - 0.39
Dy	1.73	0.03	1.76	2.03	-	-
Er	1.15	0.02	1.67	1.29	-	-
Tm	0.17	0.03	17.6	0.2	-	-
Yb	1.10	0.02	2.07	1.26	-	-

Table 6.5: REE concentrations (in ppm) for SARM-19 by HPIC analysis, compared to INAA (Willis & Hart,1985) and published data (Ring & Hansen,1984).

	HPIC	INAA	PUBLISHED DATA	
			$\bar{x}$	Range
La	33.4	25.8	27	26 - 39
Ce	55.0	56.4	56	31 - 59
Pr	5.50	6.7	-	-
Nd	18.4	26.4	-	-
Sm	3.75	4.49	4.9	4.1 - 5.0
Eu	0.65	0.70	(0.7)	0.63 - 1.02
Gd	3.27	4.3	-	-
Tb	0.51	0.65	(0.7)	0.64 - 0.79
Dy	3.20	3.62	-	-
Er	1.82	2.4	-	-
Yb	1.56	1.93	(2)	1.48 - 2.15

Table 6.6: REE concentrations (in ppm) for SARM-20 by HPIC analysis, compared to INAA (Willis & Hart,1985) and published data (Ring & Hansen,1984).

	HPIC	INAA	PUBLISHED DATA	
			$\bar{x}$	Range
La	46.3	43.6	43	40 - 63
Ce	83.8	87.8	87	45 - 88
Pr	8.49	8.5	-	-
Nd	28.7	33.6	-	-
Sm	5.49	6.22	6.3	5.8 - 6.8
Eu	1.01	1.02	(1)	0.96 - 1.18
Gd	4.90	4.5	-	-
Tb	0.85	0.91	(0.9)	0.89 - 1.23
Dy	4.74	4.80	-	-
Er	2.56	2.7	-	-
Yb	2.47	2.67	(2)	1.92 - 3.74

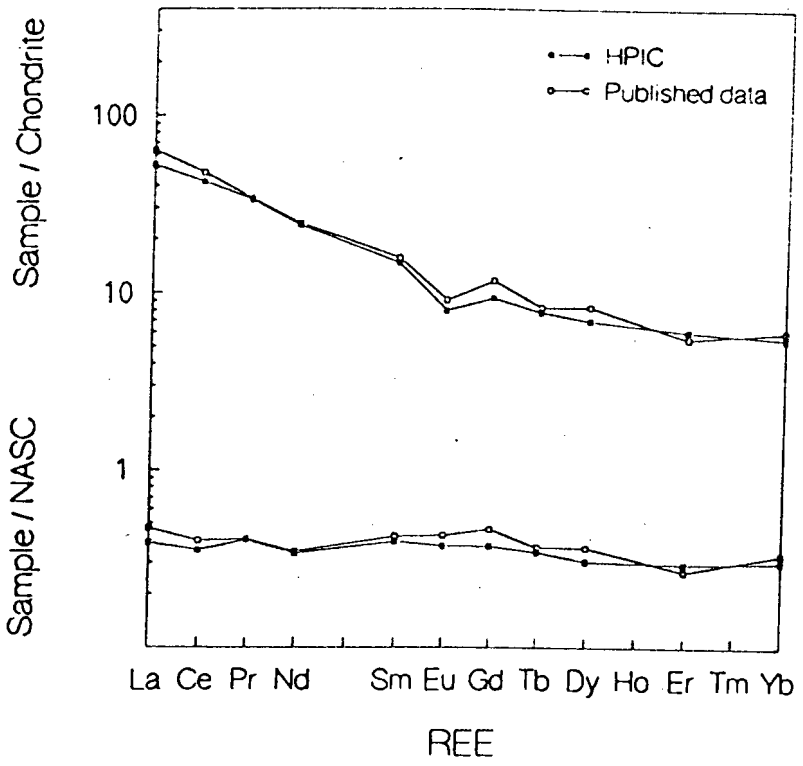


Figure 6.1: REE abundances, determined by HPIC analysis and other available techniques, of NBS-1632a normalised to chondrite and NASC values.

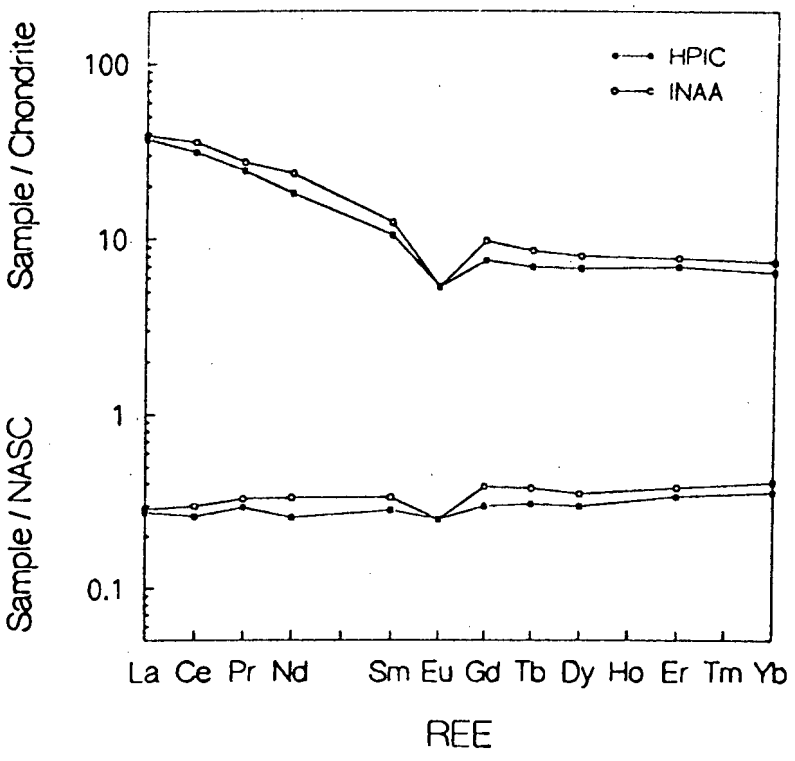


Figure 6.2: REE abundances,determined by HPIC analysis and INAA analysis, of SARM-18 normalised to chondrite and NASC values.

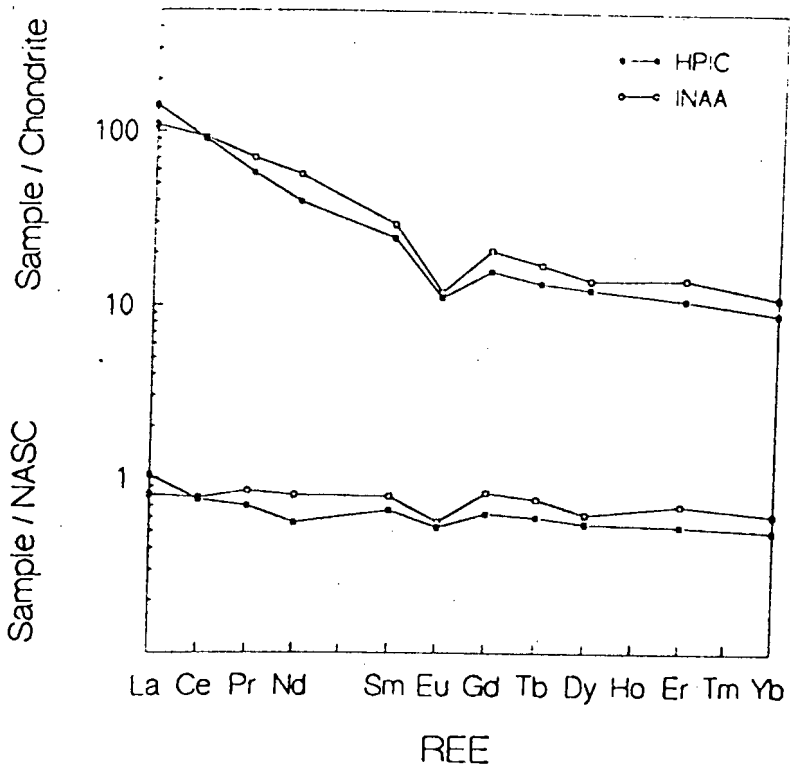


Figure 6.3: REE abundances, determined by HPIC analysis and INAA analysis, of SARM-19 normalised to chondrite and NASC values.

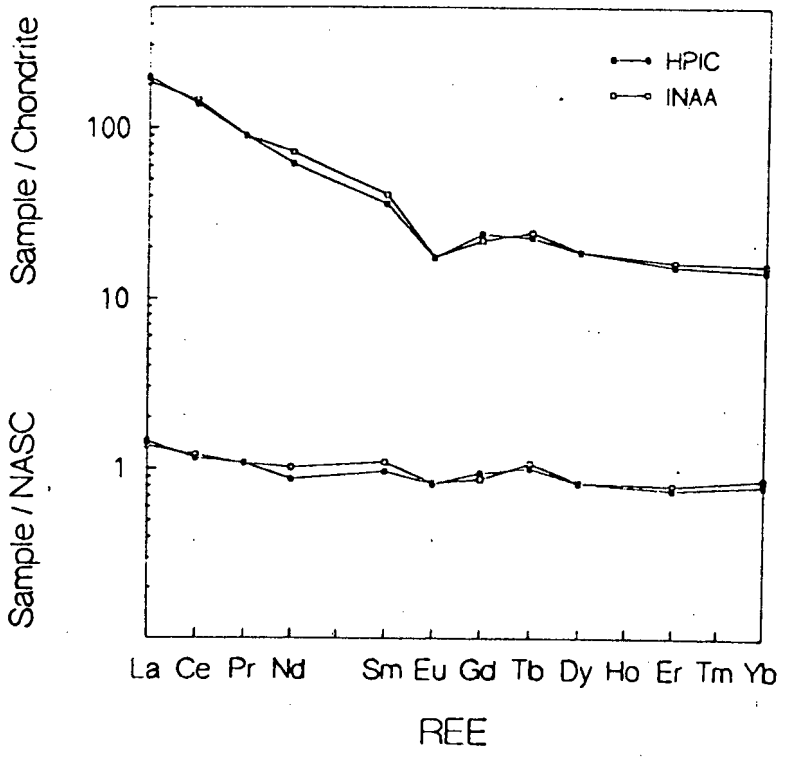


Figure 6.4: REE abundances, determined by HPIC analysis and INAA analysis, of SARM-20 normalised to chondrite and NASC values.

concentration employed in the analysis, and will be different for each element. With the conditions applied during this study, the limits of detection were in the order of 10 - 50ppb for each REE in the original coal and fly ash. For coal sample solutions, analysed using the concentrationing procedure outlined in this study, the limits of detection were in the order of 0.1 - 0.5µg/l.

6.1.3.3 *Accuracy*

Assessing the accuracy of the results from the present study is made difficult by the limited availability of REE data for the reference materials. The results of HPIC analysis for the coals NBS-1632a, SARM-18, SARM-19 and SARM-20 are compared to those obtained by INAA and available reference values in Tables 6.2, 6.4, 6.5 and 6.6 (Gladney et al.,1984; Willis & Hart, 1985).

6.1.4 DISCUSSION OF RESULTS

6.1.4.1 *Comparison of HPIC data and published data*

The REE concentrations determined from the coal reference materials in this study typically fall within the ranges of published data. INAA REE values of NBS-1632a, SARM-18, SARM-19 and SARM-20 (Willis & Hart,1985) are generally slightly higher than those obtained from HPIC analysis in this study (Tables 6.2, 6.4, 6.5 and 6.6). Exceptions are the Pr value of NBS-1632a, the La values of SARM-19 and SARM-20 and the Gd value of SARM-20.

Throughout this study greater variation in the La values than in values for the other REE was noted. The cause was determined by experimentation. It was found that low La values resulted when insufficient 4M HCl acid was used during bulk separation of the REE from the matrix elements by cation separation (Section 4.1.1), as some La was left on the separator column. The La which remained on the column was eluted with the REE of the next sample passed through the column, resulting in the second sample having a high La value. To

overcome this problem the volume of 4M HCl was increased, which prevented some La from being left on the separator column.

REE data of NBS-1632a fall within the published range (Gladney et al.,1984), though predominantly towards the lower values. Dy which is outside (lower than) the range, is the only exception (Table 6.2). Pr, by HPIC analysis, is higher than the published mean.

REE for SARM-18, SARM-19 and SARM-20 fall within the published recommended range (Ring & Hansen,1984) (Tables 6.4 to 6.6). An exception for the three SARM standards was Sm, for which the HPIC data were lower than the recommended values. The Tb values, by HPIC analysis, of SARM-19 and SARM-20 were lower than the published data. The La values of SARM-19 and SARM-20, by HPIC analysis, were slightly higher than the published mean.

6.1.4.2 *Chondrite and NASC Normalised REE Plots*

There is general agreement that the bulk earth has a REE pattern essentially the same as C1 carbonaceous chondrite meteorites (McLennan,1989). Therefore, the REE pattern of a sample normalised to chondritic REE concentrations may indicate the effects of partial melting and fractionation, hence giving some indication of the sample's petrogenetic history. Sedimentary REE patterns may reflect their average provenance composition. The North American Shale Composite (NASC) is frequently used for normalising sedimentary samples, as the REE pattern of the average shale is thought to parallel that of the average upper continental crust (McLennan,1989).

Smooth, coherent chondrite normalised REE plots from the HPIC data, and flat patterns produced when normalised to the NASC values, provide some indication of the coherence of the data produced by the technique (Figs. 6.1 to 6.4).

The HPIC REE normalised patterns are smoother than the published data and INAA patterns (Figs. 6.1 to 6.4), and therefore probably indicate more internally consistent values. Fluctuations on normalised patterns between individual REE should not occur because of the

closely coupled behaviour of the lanthanides in geological processes. When the REE values of NBS-1632a were normalised to chondrite values the heavy REE data from published values had a slightly steeper slope than data from HPIC analysis (Fig.6.1).

Normalised patterns of data from HPIC and INAA analysis of SARM-18 were approximately parallel (Fig.6.2). When the REE data of SARM-19 were normalised to chondrite and NASC values the slope of the light REE (La to Nd) for the HPIC data was steeper than the slope of the INAA data (Fig.6.3). The normalised patterns for HPIC and INAA analysis of SARM-20 are similar. The Eu anomaly from INAA data is greater than from the HPIC data for SARM-18 and SARM-19 (Figs.6.2 and 6.3). The Pr values on NASC normalised patterns, for the four samples analysed, were slightly high relative to the neighbouring Ce and Nd points.

6.2 RARE EARTH ELEMENT DETERMINATION OF USGS CLB-1

Following the successful determination of REE in Standard Reference Materials, the technique was applied to the determination of REE in a new reference coal sample, USGS CLB-1. The sample was provided by Dr. J.Kane of the USGS, in three bottles each containing ~500g whole coal. CLB-1 is a very low ash, low REE coal with an ash content of 6.32% (Dr. J.Kane, *pers.comm.*)

6.2.1 SAMPLE PREPARATION AND HPIC ANALYSIS

Five separate sample solutions were prepared, by microwave digestion, for each of the three CLB-1 bottles. Two of the sample solutions were spoiled during preparation and were discarded. On-line concentration of 5ml of sample solution was necessary for suitable REE detection levels to be obtained. The samples were analysed in duplicate in random sequence, with a REE standard solution run after each sample.

6.2.2 DATA

The following data are presented:

1. REE concentrations for individual sample solutions of each of the three bottles are given in Table 6.7.

2. Mean REE concentrations for CLB-1 compared to provisional data (Dr. J.Kane, *pers.comm.*) - Table 6.8.

3. Chondrite and NASC normalised plots of CLB-1 from HPIC data, compared to the provisional data - Figure 6.5.

6.2.3 DISCUSSION

6.2.3.1 *REE Analysis*

The reproducibility for individual REE, between sample solutions from individual bottles, was generally <5%CoV (Table 6.7). Significantly poorer precision was obtained for Tm, due to Tm concentration levels being close to the lower limit of detection (Section 6.1.3.1). Two of the three bottles of CLB-1 coal provided, bottles 1179 and 1187, showed similar variation between individual samples, effectively indicating homogeneity. However, greater variation was observed for bottle 1136.

An increase in the CoV of La, Eu, Nd, Tm and Yb was recorded for bottle 1136 (Table 6.7). A greater variation in composition within bottle 1136 compared to 1179 and 1187 was also recognised for some major oxides (SiO_2, Al_2O_3, CaO and P_2O_5) and some trace elements during XRFS analysis (Prof. J.P.Willis, *pers.comm.*). The greatest variation amongst the trace elements was for Sr. Increased variation in XRFS results for bottle 1136 was attributed to elevated concentrations of each of the above oxides and Sr in one of three briquettes.

Table 6.7: Replicate analyses of REE concentrations (in ppm) from three bottles of USGS CLB-1, determined by HPIC analysis.

CLB-1 (1179) (n=4)							
	1	2	3	4	$\bar{x}$	sd	%CoV
La	5.16	4.94	5.28	5.21	5.14	0.14	2.78
Ce	10.5	10.4	10.8	10.6	10.6	0.20	1.86
Pr	1.26	1.33	1.37	1.36	1.35	0.07	5.05
Nd	4.91	4.75	5.03	4.78	4.87	0.13	2.60
Sm	1.00	0.96	0.98	0.92	0.95	0.06	6.62
Eu	0.21	0.21	0.23	0.22	0.22	0.01	3.06
Gd	0.97	0.88	0.96	0.93	0.94	0.04	3.94
Tb	0.15	0.15	0.15	0.15	0.15	0.003	1.99
Dy	0.93	0.91	0.92	0.92	0.92	0.01	1.25
Er	0.55	0.53	0.54	0.57	0.54	0.01	2.14
Tm	0.08	0.09	0.07	0.09	0.08	0.01	12.05
Yb	0.51	0.47	0.49	0.51	0.49	0.02	3.86

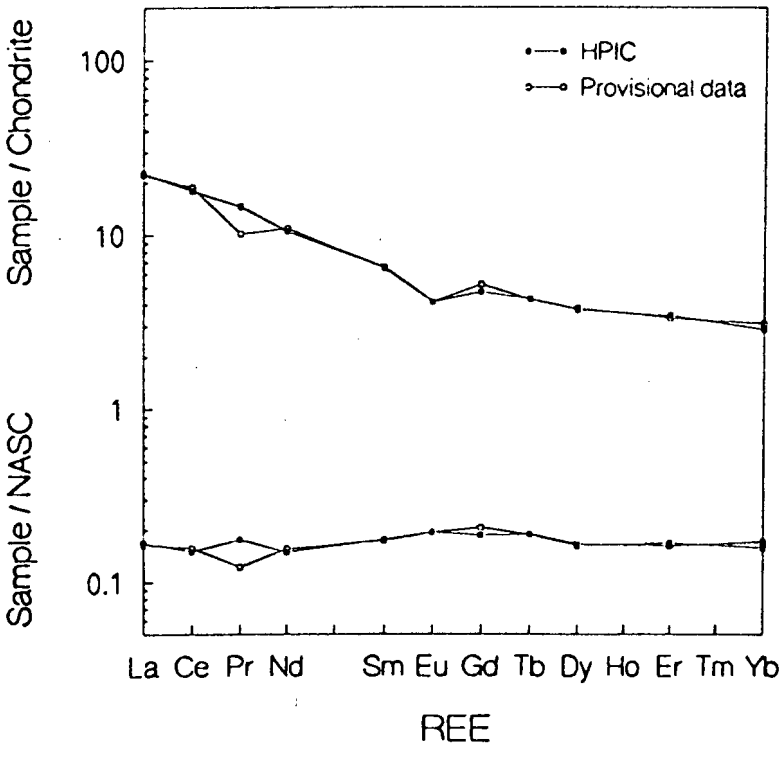
CLB-1 (1187) (n=5)								
	1	2	3	4	5	$\bar{x}$	sd	%CoV
La	5.34	5.19	5.43	5.53	5.40	5.38	0.12	2.30
Ce	10.9	10.9	11.3	11.1	11.7	11.2	0.31	2.78
Pr	1.37	1.36	1.50	1.50	1.42	1.43	0.07	4.81
Nd	5.25	-	-	4.91	4.86	5.01	0.21	4.19
Sm	1.03	1.04	1.01	1.01	1.07	1.03	0.02	2.26
Eu	0.23	0.23	0.24	0.21	0.24	0.23	0.01	5.63
Gd	0.94	0.99	1.03	0.96	1.02	0.99	0.04	3.85
Tb	0.16	0.15	0.17	0.16	0.17	0.16	0.01	3.02
Dy	0.97	0.96	0.98	0.97	0.99	0.97	0.01	1.44
Er	0.56	0.58	0.63	0.59	0.61	0.59	0.03	4.38
Tm	0.09	0.09	0.09	0.09	0.09	0.09	0.003	3.12
Yb	0.52	0.50	0.53	0.52	0.51	0.51	0.01	2.14

CLB-1 (1136) (n=4)							
	1	2	3	4	$\bar{x}$	sd	%CoV
La	5.84	5.90	5.42	5.32	5.62	0.29	5.16
Ce	11.1	11.6	11.3	11.1	11.3	0.24	2.13
Pr	1.31	1.49	1.43	1.35	1.40	0.08	5.81
Nd	4.84	5.41	4.48	4.74	4.87	0.39	8.10
Sm	1.00	1.05	1.03	0.98	1.02	0.03	2.75
Eu	0.28	0.33	0.26	0.23	0.27	0.04	16.12
Gd	0.96	1.04	1.00	1.00	1.00	0.03	3.11
Tb	0.15	0.17	0.16	0.16	0.16	0.01	3.77
Dy	0.89	0.95	0.97	0.96	0.94	0.04	3.72
Er	0.57	0.57	0.60	0.57	0.58	0.01	2.08
Tm	0.10	0.10	0.06	0.09	0.09	0.02	21.04
Yb	0.41	0.49	0.47	0.50	0.47	0.04	8.97

Table 6.8: REE concentrations (in ppm), determined by HPIC analysis, of USGS CLB-1, compared to provisional data. (n=3)

	HPIC			Dr. J.Kane (pers.comm.)		
	$\bar{x}$	sd	%CoV	$\bar{x}$	n	Range
La	5.38	0.24	4.43	5.28	11	2.70 - 6.22
Ce	11.0	0.36	3.30	11.51	12	8.48 - 19.44
Pr	1.39	0.04	3.04	0.97	2	0.58 - 1.36
Nd	4.91	0.08	1.62	5.12	8	3.87 - 5.89
Sm	1.00	0.04	4.32	0.99	6	0.34 - 1.25
Eu	0.24	0.03	12.31	0.24	7	0.22 - 0.26
Gd	0.97	0.03	3.38	1.07	2	1.02 - 1.13
Tb	0.16	0.01	3.37	0.16	7	0.14 - 0.20
Dy	0.94	0.03	2.71	0.96	1	-
Er	0.57	0.03	4.40	0.55	1	-
Tm	0.09	0.003	3.71	0.08	2	0.08 - 0.09
Yb	0.49	0.02	4.89	0.53	9	0.41 - 0.74

Figure 6.5: REE abundances, determined by HPIC analysis of CLB-1 normalised to chondrite and NASC values, compared with provisional data.



The agreement between the average values for each of the bottles was <5%CoV, with the exception of Eu (Table 6.8). The greater relative error recorded in the analysis of Eu (12.31%CoV) results from the Eu values of bottle 1136 being significantly higher (17%) than either of the other bottles. Eu is preferentially concentrated in plagioclase feldspar ($CaNaAl_2Si_2O_8$). Slight enrichment of this mineral in the ash fraction of the coal in bottle 1136 would account also for elevated values of SiO_2, Al_2O_3, CaO and Sr. Variations in P and Sr might similarly be explained by a slight difference in the amount of apatite ($CaPO_4$) in the sample. Clearly a degree of heterogeneity in the mineral content of bottle 1136 was indicated. Despite the greater degree of variation for some of the REE, from bottle 1136, the mean values obtained for the lanthanide elements from this bottle are little different from the mean values of the other bottles.

6.2.3.2 *Comparison of HPIC data and Provisional Data*

The results for CLB-1 generally compare closely to the provisional mean of values obtained from other laboratories (Dr. J.Kane, *pers.comm.*) (Table 6.8). Twelve laboratories provided data for the provisional REE values. Only one laboratory, listed in the provisional data provided by Dr. J.Kane, reported values for all the REE that were analysed by HPIC in this study. Two HPIC REE values fell outside the provisional range. Gd was lower than the range while Pr was higher (Table 6.8). However, only two laboratories reported Pr values, one of which compares closely with the HPIC data. Comparisons between the HPIC data and mean values calculated from the provisional data improve when outlier values are excluded from the provisional data.

Normalised patterns for both the HPIC data and the provisional data (Fig.6.5) compare well, with Pr being a notable exception. The low provisional Pr value is reflected by a dip on the normalised plots. Both HPIC normalised plots are highly coherent and smooth.

CHAPTER 7

DETERMINATION OF REE IN ASHED COAL

Ashing is typically used for the removal of organic matter from coal samples, prior to their dissolution. To test the reliability of the microwave dissolution technique, coal samples were prepared by ashing prior to analysis by HPIC. The resultant data were compared with data from Chapter 6, which were obtained using the microwave dissolution technique.

7.1 REFERENCE MATERIALS

To enable direct comparison between REE values obtained following microwave digestion and ashing, three Standard Reference Materials previously prepared by the microwave dissolution technique - SARM-18, SARM-19 and SARM-20, were prepared by ashing. The ash content of these coals ranged from 9.9% ash (SARM-18) to 35.3% ash (SARM-20).

7.2 SAMPLE PREPARATION AND ANALYSIS

Ash was prepared by the two ashing procedures outlined in Section 3.1.4.1 (Table 3.2). Procedure 1 ("fast ashing") was the ashing procedure used by Bosch (1990) and Lenahan & Murray-Smith (1986). Procedure 2 ("slow ashing") was a modified procedure in which the intervals between successive temperature increases were lengthened. Intervals of 15 or 30 minutes in procedure 1, were increased to 1 hour in procedure 2. Sufficient ash was prepared, from each of the two ashing procedures, to enable HPIC, X-Ray Diffraction (XRD) and XRFS analysis.

7.2.1 REE ANALYSIS BY HPIC

Four sample solutions, two from each ashing procedure, were prepared of SARM-18, SARM-19 and SARM-20. The dissolution procedure outlined in section 3.2.1.1. was used to prepare the sample solutions. The ashed coal was fused with Li-borate flux and then dissolved in

0.4M HCl. Each sample solution was analysed in duplicate. The larger sample size of ~0.5g ash, equivalent to >3g of whole coal, provided sufficient REE for accurate determination to be possible by direct sample injection via a sample loop of 100µl.

7.2.2 X-RAY DIFFRACTION ANALYSIS

Ash of each of the three samples, prepared by both ashing procedures was analysed. Ashed sample, ground using a pestle and mortar, was loaded into a perspex sample holder. CuKα radiation, at 30mA and 40kV was used to irradiate the samples. Scans from 3-15°2θ were made using 1/2° divergent and receiving slits, then from 15.1-65°2θ using 1° divergent and receiving slits.

7.2.3 X-RAY FLUORESCENCE SPECTROMETRY ANALYSIS

Ash from both ashing procedures, for each of the coal samples, was formed into briquettes. The briquettes comprised 1g of ashed coal and 3g of acid washed SiO_2 powder, which were mixed for 30 minutes in a Turbula® mixer mill. A few drops of Mowiol solution (2% Hoechst N 70-80 in distilled water) were used as a binder. The samples were pressed into 30mm diameter pellets with boric acid backing at 7 tons pressure on ram. The briquettes were analysed to determine the concentration of 4 trace elements, Zn, Cu, Ni and Ga (section 7.4.3).

7.3 DATA

1. REE values for SARM-18, SARM-19 and SARM-20 prepared for HPIC analysis after ashing were compared to results for the samples after microwave digestion and to published data - Tables 7.1 to 7.3.

2. XRFS values for Zn, Cu, Ni and Ga in SARM-18, SARM-19 and SARM-20 following ashing by procedures 1 and 2 are given in Table 7.4.

3. Histograms of REE values, from the two ashing procedures and microwave digestion, for SARM-18, SARM-19 and SARM-20 are given in Figure 7.1.

4. Chondrite normalised REE plots for SARM-18, SARM-19 and SARM-20, comparing data from both ashing procedures and microwave digestion values are given in Figures 7.2 to 7.4.

7.4 DISCUSSION

7.4.1 REE ANALYSIS

The light REE (La to Pr) concentrations determined for samples prepared after ashing procedure 1 were generally significantly lower than the values determined after microwave digestion. The percentage difference between the two dissolution techniques was typically greater than 5% for the light REE. In the modified ashing procedure 2 (Table 3.2) there was a reduced possibility of smoke production and loss of particulate matter. However, the REE concentrations determined after ashing procedure 2 still differed, but to a lesser degree, from those determined following microwave digestion. There were significant differences in REE concentrations between the two ashing procedures.

The REE concentrations of SARM-18 following ashing by the faster ashing procedure were greater than those for the slower ashing procedure, except for La and Eu (Fig.7.1). Typically the percentage difference between the two procedures was less than 5%, with the exception of La and Nd (15% and 8% respectively) (Table 7.1). The La value for SARM-18, from ashing procedure 2, was high. High La values may result from contamination following sample preparation in a laboratory routinely using La-bearing flux (section 3.1.5), or from the cation separation column, used for matrix removal, still containing La from a previous sample (section 6.1.4.1).

The trend observed for SARM-18 was reversed for SARM-19 and SARM-20, with the percentage differences between the two procedures being significantly greater for SARM-19 than SARM-20 (Tables 7.2 and 7.3, Fig.7.1). For SARM-19 the percentage difference

Table 7.1: REE concentrations (in ppm), determined by HPIC analysis, for SARM-18 prepared by microwave dissolution and the two ashing procedures. The published range of Ring & Hansen (1984) and the 2 sigma range is shown.

	MICROWAVE DISSOLUTION	ASHING		MICROWAVE RANGE	PUBLISHED RANGE
		PROCEDURE 1	PROCEDURE 2	2 SIGMA	
La	8.79	8.33	9.74	8.33 - 9.25	9 - 16
Ce	19.1	18.2	18.1	18.4 - 19.7	12 - 24
Pr	2.32	2.10	2.04	2.24 - 2.40	
Nd	8.49	8.17	7.54	8.29 - 8.69	
Sm	1.61	1.64	1.60	1.43 - 1.79	1.8 - 2.2
Eu	0.31	0.28	0.29	0.30 - 0.32	0.29 - 0.41
Gd	1.55	1.59	1.52	1.47 - 1.63	
Tb	0.26	0.27	0.26	0.25 - 0.27	0.19 - 0.39
Dy	1.73	1.72	1.70	1.67 - 1.79	
Er	1.15	1.14	1.11	1.11 - 1.19	
Yb	1.10	1.12	1.09	1.06 - 1.14	
% ASH	-	9.4	9.4	-	-

Table 7.2: REE concentrations (in ppm), determined by HPIC analysis, for SARM-19 prepared by microwave dissolution and the two ashing procedures. The published range of Ring & Hansen (1984) and the 2 sigma range is shown.

	MICROWAVE DISSOLUTION	ASHING		MICROWAVE RANGE	PUBLISHED RANGE
		PROCEDURE 1	PROCEDURE 2	2 SIGMA	
La	33.4	22.4	25.4	32.9 - 33.9	26 - 39
Ce	55.0	46.6	49.7	54.4 - 55.6	31 - 59
Pr	5.50	4.85	5.32	5.42 - 5.58	
Nd	18.4	18.3	18.0	18.2 - 18.6	
Sm	3.75	3.48	3.93	3.57 - 3.93	4.1 - 5.0
Eu	0.65	0.63	0.70	0.64 - 0.66	0.63 - 1.02
Gd	3.27	3.20	3.39	3.19 - 3.35	
Tb	0.51	0.53	0.55	0.50 - 0.52	0.64 - 0.79
Dy	3.20	3.20	3.53	3.14 - 3.26	
Er	1.82	1.86	1.98	1.78 - 1.86	
Yb	1.56	1.76	1.72	1.52 - 1.60	1.48 - 2.15
% ASH	-	26.5	26.6	-	-

Table 7.3: REE concentrations (in ppm), determined by HPIC analysis, for SARM-20 prepared by microwave dissolution and the two ashing procedures. The published range of Ring & Hansen (1984) and the 2 sigma range is shown.

	MICROWAVE DISSOLUTION	ASHING		MICROWAVE RANGE	PUBLISHED RANGE
		PROCEDURE 1	PROCEDURE 2	2 SIGMA	
La	46.3	37.7	41.2	45.8 - 46.8	40 - 63
Ce	83.8	73.4	77.5	83.2 - 84.4	45 - 88
Pr	8.49	7.74	7.90	8.41 - 8.57	
Nd	28.7	28.1	26.6	28.5 - 28.9	
Sm	5.49	5.24	5.29	5.31 - 5.67	5.8 - 6.8
Eu	1.01	0.88	0.99	1.00 - 1.02	0.96 - 1.18
Gd	4.90	4.60	4.69	4.82 - 4.98	
Tb	0.85	0.78	0.75	0.84 - 0.86	0.89 - 1.23
Dy	4.74	4.69	4.57	4.68 - 4.80	
Er	2.56	2.58	2.60	2.52 - 2.60	
Yb	2.47	2.32	2.32	2.43 - 2.51	1.92 - 3.74
% ASH	-	32.8	32.9	-	-

Table 7.4: XRFS data (in ppm) for coal samples ashed by procedures 1 and 2 (fast and slow ashing respectively), compared with the recommended values (Ring & Hansen,1984).

	SARM-18			SARM-19			SARM-20		
	R.V.	Fast	Slow	R.V.	Fast	Slow	R.V.	Fast	Slow
Zn	5.5	5.5	5.5	12	16	15	17	23	21
Cu	5.9	4.7	4.2	13	9.8	11	18	13	14
Ni	10.8	11	11	16	15	20	25	25	25
Ga	(8)	6.1	6.3	14	10	9.6	16	12	12

R.V. - Recommended Value

(*) - Suggested Value

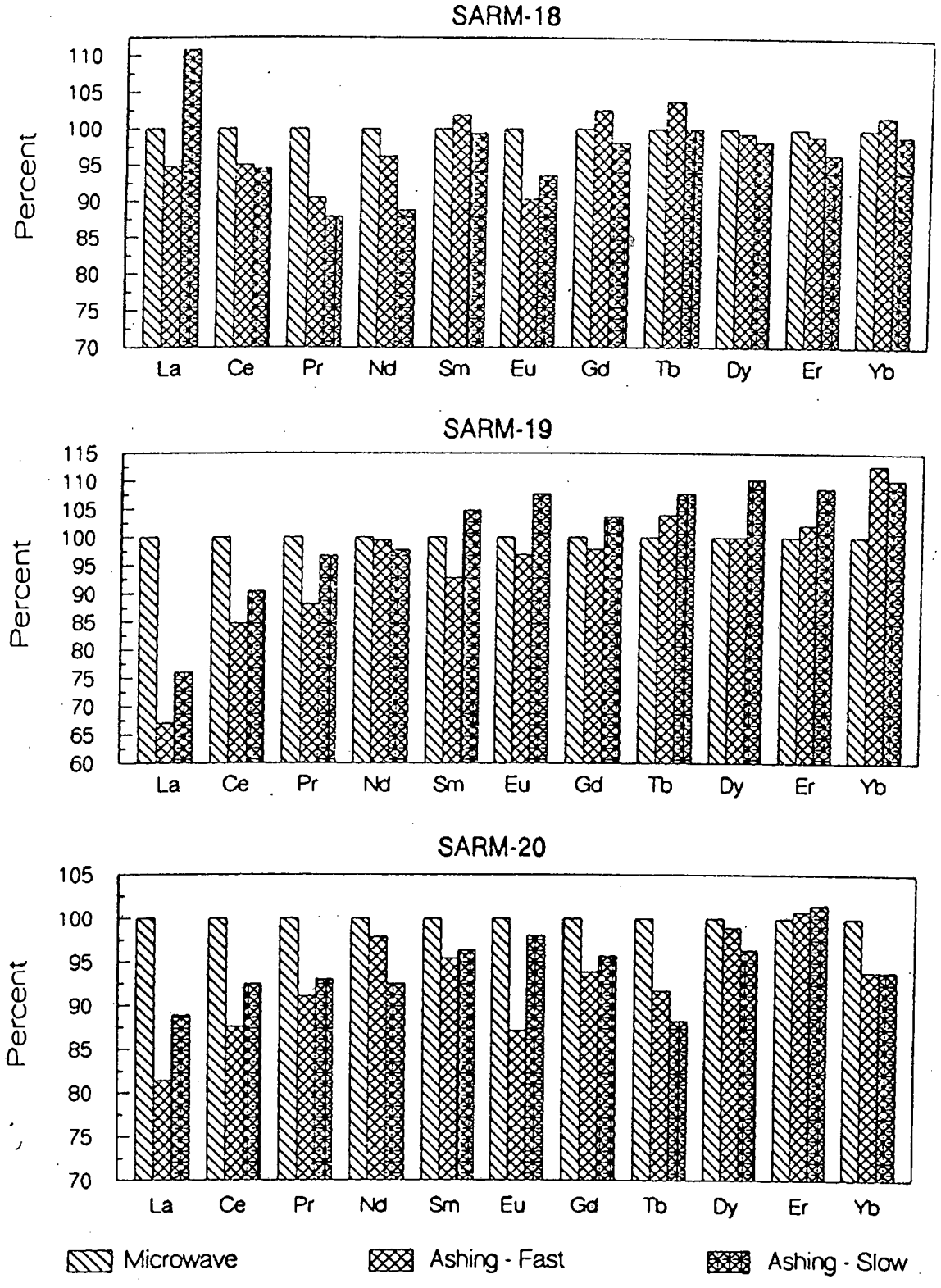


Figure 7.1: REE data of SARM-18, SARM-19 and SARM-20 are presented as histograms. The REE values from the two ashing procedures are expressed as a percentage of the REE values determined following microwave digestion (i.e. microwave data are 100%).

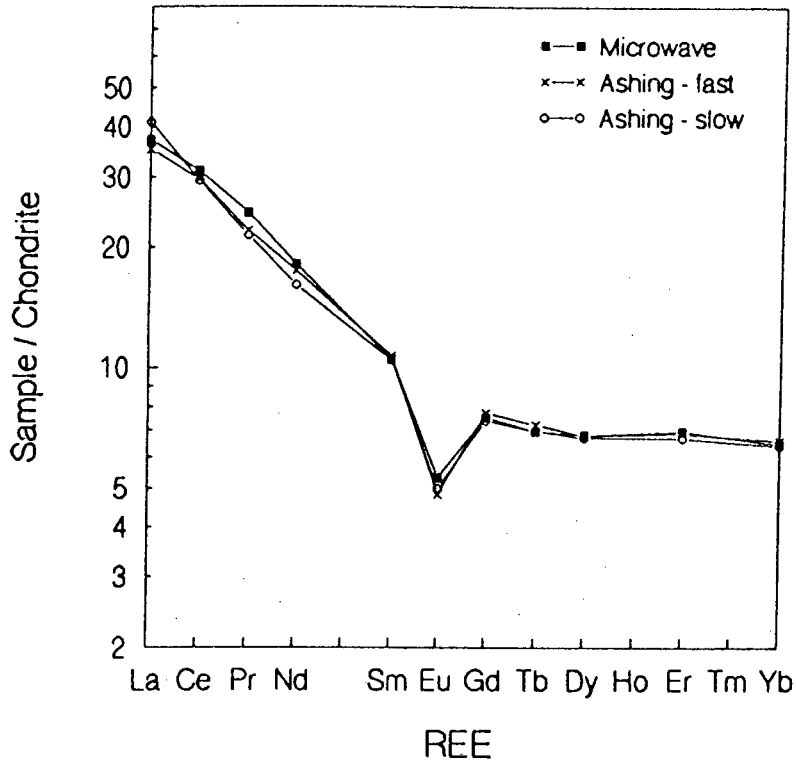


Figure 7.2: REE abundances determined by HPIC analysis, after microwave digestion and ashing, of SARM-18 normalised to chondrite values.

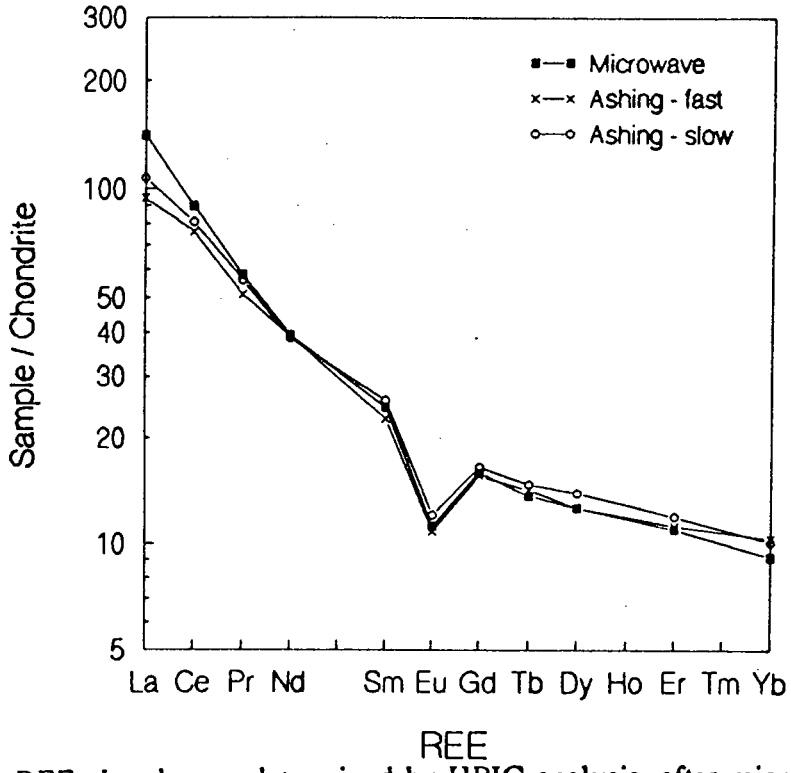


Figure 7.3: REE abundances determined by HPIC analysis, after microwave digestion and ashing, of SARM-19 normalised to chondrite values. Note the decrease in the slope of the light REE after ashing.

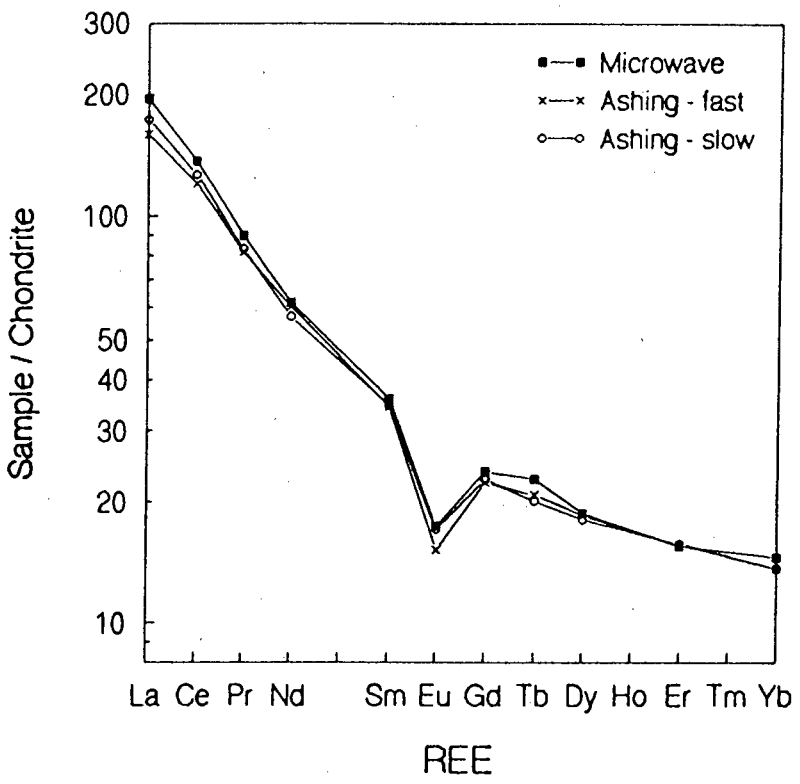


Figure 7.4: REE abundances determined by HPIC analysis, after microwave digestion and ashing, of SARM-20 normalised to chondrite values. Note the decrease in the slope of the light REE after ashing.

between the ashing procedures was typically greater than 5%, ranging from 6% to 12%. Exceptions were Tb and Yb, with less than 4% difference between the procedures. Only Nd and Yb concentrations of procedure 2 were less than procedure 1 (Table 7.2, Fig.7.1). Typically, for SARM-20 less than 5% difference was recorded, except for Eu and La, between the ashing procedures. The Nd, Tb and Dy concentrations of procedure 2 were less than those of procedure 1 (Table 7.3).

The 2 sigma range, of individual REE, for each of the samples prepared by microwave digestion were determined, in order to evaluate the significance of REE concentration differences between samples prepared by microwave dissolution and after ashing. The light REE concentrations from the ashing techniques were typically less than the lower limits of the 2 sigma ranges. Some REE values, from microwave digestion and ashing, were less than the lower limits of published data (Tables 7.1 to 7.3).

The light REE and Eu of SARM-18, from both ashing procedures, were less than the 2 sigma range. Only La from procedure 2 was greater than the 2 sigma range. Similarly the light REE concentrations of SARM-19 were less than the 2 sigma range. Generally the intermediate and heavy REE concentrations (Sm to Yb) of ashing procedure 2 were higher than the upper 2 sigma range, but for procedure 1 only Tb and Yb exceeded the range. For SARM-20, the light REE of both ashing techniques were typically below the lower 2 sigma range.

The differences discussed above between the two ashing procedures and between the ashing and microwave dissolution procedures, are reflected in chondrite REE normalised plots (Figs. 7.2 to 7.4). Changes in the slope of the light REE on the chondrite normalised plots of SARM-19 and SARM-20 reflect the differences between the three procedures (Figs. 7.3 and 7.4).

7.4.2 XRD ANALYSIS

Ash, from both ashing procedures, was analysed by X-ray diffraction in an attempt to determine the cause of differences in REE concentrations, recorded after the different ashing

procedures. Only two minerals, quartz and mullite, and glass were identified in all samples. When SARM-18, SARM-19 and SARM-20 were ashed at a lower temperature than used during the present study, by Dr. M.Palmer at the Geology Department, University of Western Ontario, quartz, kaolinite, calcite, dolomite and hematite were identified by XRD analysis, so giving some indication of the mineralogy in the original coal.

The mullite, in the ashed coal, would have been derived by the breakdown of kaolinite in the original coal (Brindley & Nakahira,1959). At approximately 500°C kaolinite is altered to metakaolinite by the loss of structural water, then at 950-1000°C rapid recrystallization of the metakaolinite to mullite occurs, at this point rehydration will not alter the crystal form (Brindley & Nakahira,1959; Deer, Howie & Zussmann,1982).

7.4.3 XRFS ANALYSIS

XRFS analysis of each of the ash samples was performed in an attempt to determine whether other trace elements (Zn, Cu, Ni and Ga) behaved like the REE when ashed (Table 7.4). Zn, Cu and Ni were selected for analysis as they are non-volatile, therefore, it was expected that they would behave like the REE. Ga was selected as it is volatile and is present in clay minerals (Cotton & Wilkinson,1980). Therefore, Ga might be lost if clay minerals were broken down during ashing, and would be lost with the particulate matter (clays) if smoke was produced.

XRFS data for the ashed samples are compared to their recommended values in Table 7.4. The concentrations of the elements analysed, in the coal ash, were well above their XRFS detection limits. The Ni values following both ashing procedures were the same as the recommended values. The only exception was SARM-19, procedure 2, which had a considerably higher Ni value than the recommended value. Following ashing the Cu values were typically 20% less than the recommended values. For SARM-18 the Cu value of procedure 2 was less than that of procedure 1. For SARM-19 and SARM-20 the procedure 2 values were greater than procedure 1. The same trend was observed for the REE data, from HPIC analysis, between the two ashing procedures. Following ashing of SARM-18 the Zn values were the same as the recommended value. However, for SARM-19 and SARM-20 the

Zn values were higher than the recommended values. The Ga values following ashing were less than the recommended values, as would be expected for a volatile element. The difference between the recommended values and ashed values was ~25%.

7.4.4 POSSIBLE CAUSES FOR THE LOSS OF REE DURING ASHING

The purpose of ashing coal prior to its dissolution is to remove the coal's carbon content. With temperature increase the carbon combines with O_2 to form CO_2 and is lost to the atmosphere. During breakdown of the organic component of coal, metals (including REE) may be liberated that are complexed with the organics (Bouška,1981), or may be liberated from mineral matter included in the organic fraction. If the production of smoke (smoking) is avoided during ashing only the organic components of the coal should be lost. Volatile elements may be lost due to the high temperature attained during ashing (950°C). However, loss of the REE during ashing was unexpected as they are only volatilized at temperatures in excess of 2000°C (Weast,1975). Therefore, the REE should not have been lost by volatilization, but were probably lost as particulate matter. In the present study smoking may have occurred during the fast ashing procedure, but should have been limited during the slower ashing technique, so accounting for the greater loss of elements following ashing procedure 1.

During ashing mullite forms from the breakdown of kaolinite (Brindley & Nakahira,1959). Any REE associated with the kaolinite may be liberated during the recrystallization process and lost as particulate matter. If some REE bearing minerals were incorporated as extremely fine grains within the organic fraction of the coals, e.g. clay minerals and phosphates, they may have been liberated during ashing as particulate matter. This would account for differences in REE levels between ashing and microwave digestion, as a sealed vessel was used during microwave digestion, therefore preventing the loss of particulate matter.

No mineral contains a single REE, but contains all the REE in varying concentrations. Therefore, each REE would have been lost to some extent during the production of smoke. To account for the observed decrease in light REE in the present study, some light REE

enriched mineral, which is readily volatilised, e.g. a phosphate, must have been lost. The loss of light REE enriched minerals would account for the chondrite patterns observed (Figs. 7.2 to 7.4), i.e. the pattern of the ashed samples have low light REE values relative to those of microwave digested samples, but have the same heavy REE slopes. However, the increase in heavy REE observed for procedure 2 of SARM-19 is not explained.

CHAPTER 8

REE ANALYSIS OF FLY ASH

During the combustion process (~1300°C) of pulverised coal at coal burning power stations, the inorganic component of the coal undergoes heating, melting, vaporisation and new mineral growth. The residue resulting from these processes is pulverised fuel ash (PFA). PFA comprises fly ash which is removed with the flue gas, and bottom ash which is collected from the bottom of the combustion chamber.

Fly ashes generally contain concentrations of REE equal to, or greater than, those present in natural rocks. Consequently, the analysis of their REE content may be routinely performed by HPIC analysis. REE determination by anion separation, following Li-borate fusion, in international Standard Reference Materials (SRMs) and in-house standard samples was performed to test the accuracy and precision of the analytical procedure. The analytical technique was then applied to fly ash samples from two South African power stations, to determine the behaviour of REE following combustion of coal.

8.1 REFERENCE MATERIALS

A fly ash sample from Matla power station, in the Transvaal, was used to determine the reproducibility of the analytical procedure. The sample had previously been analysed by XRFS (Bosch,1990). As no published REE data for fly ash SRM samples were available, igneous silicate rock standards were used to determine the accuracy of the technique. An international standard, SY-2, was selected as it has similar REE concentrations to fly ash. Two in-house powdered rock standards, ALR33G and TDC-77, were also analysed. The REE concentrations of three international SRM fly ashes, NBS-2689, NBS-2690 and NBS-2691, were determined. However, the accuracy of the data can only be gauged by the coherent chondrite and NASC normalised REE patterns obtained from the data.

8.1.1 SAMPLE PREPARATION AND HPIC ANALYSIS

Five sample solutions of the Matla fly ash sample were prepared to determine the precision of the Li-borate fusion/dissolution and HPIC analytical technique. Single sample preparations and analyses of SY-2, ALR33G and TDC-77 were performed, to determine the accuracy of the analytical technique. Two sample solutions were prepared for each of the SRM fly ashes, NBS-2689, NBS-2690 and NBS-2691; each solution was analysed in duplicate.

For each of the samples analysed a sample solution volume of 100µl was directly injected onto the separator column. A REE standard solution was run after each sample.

A flux blank was prepared using the Li-borate fusion/dissolution procedure and the solution was analysed for REE by HPIC using the same conditions as outlined above. A chromatogram devoid of peaks was obtained indicating the absence of any significant REE contamination from the flux. The samples had to be prepared in a laboratory routinely used for the preparation of glass discs, employing a lanthanum doped flux, for XRFS. To overcome possible contamination by La, the samples and flux were weighed in a different laboratory and a Pt crucible and tongs were reserved exclusively for REE sample preparation.

8.1.2 DATA

The following data are presented:

1. Reproducibility of REE concentrations in fly ash from Matla power station are given in Table 8.1.

2. REE concentrations for international and in-house standards (SY-2, ALR33G and TDC-77) by HPIC analysis, compared to published data and data from alternative analytical procedures - Table 8.2.

3. REE concentrations for NBS-2689, NBS-2690 and NBS-2691 are given in Table 8.3.

4. Chondrite normalised REE plots for SY-2, ALR33G and TDC-77G are given in Figures 8.1 to 8.3.

5. Chondrite and NASC normalised REE plots for NBS-2689, NBS-2690 and NBS-2691 are given in Figure 8.4.

8.1.3 DISCUSSION

8.1.3.1 *Precision*

The reproducibility associated with the entire procedure of fly ash analysis is indicated by the standard deviation and %CoV of the results from the five analyses of the Matla fly ash sample (Table 8.1). Precision for each element was generally <6%CoV, with only Eu (8.3%) showing greater relative error. Tm was not recorded, since its concentration was close to the lower detection limit.

8.1.3.2 *Accuracy*

As limited data were available for the standard reference materials it was difficult to assess the accuracy of the REE concentrations determined by HPIC analysis. HPIC values for SY-2 compare favourably with accepted values (Table 8.2) (Govindaraju,1984). The REE values for the two in-house standards could only be compared with values determined by HPIC, following the routine sample preparation by HF/$HClO_4$ acid dissolution for silicate rocks (Table 8.2) (le Roex & Watkins,1990). The REE values determined after Li-borate fusion/dissolution compare closely with those obtained after acid dissolution.

8.1.3.3 *Chondrite and NASC Normalised REE Plots*

The chondrite normalised REE patterns for the REE data determined for silicate rocks during this study, and patterns from published and alternative data (Govindaraju,1984; le Roex & Watkins,1990), for the same samples compare closely (Figs. 8.1 to 8.3). The plots are highly coherent, so providing some gauge of the accuracy of the data.

Table 8.1: Reproducibility of REE data (in ppm), by HPIC analysis, for a fly ash sample from Matla power station, prepared by Li-borate fusion/ dissolution. XRFS data from Bosch (1990).

	1	2	3	4	5	$\bar{x}$	sd	%CoV	XRFS
La	120	121	119	119	112	118	3.38	2.86	100
Ce	241	243	238	234	238	239	3.29	1.38	214
Pr	27.7	27.7	25.3	25.1	27.3	26.6	1.31	4.92	
Nd	96.0	101	91.1	87.4	89.5	92.9	5.32	5.73	101
Sm	18.9	19.7	17.7	17.4	17.9	18.3	0.96	5.24	
Eu	3.21	3.60	2.91	3.10	3.42	3.25	0.27	8.31	
Gd	15.9	16.8	15.4	15.4	15.8	15.9	0.58	3.66	
Tb	2.55	2.74	2.57	2.46	2.53	2.57	0.10	3.89	
Dy	15.4	15.8	14.8	14.8	15.4	15.2	0.45	2.96	
Er	8.46	8.68	8.44	8.16	8.53	8.45	0.19	2.25	
Yb	8.04	7.88	8.07	7.97	7.75	7.94	0.13	1.64	

Table 8.2: REE data (in ppm) for international and in-house standards using Li-borate fusion/dissolution and HPIC analysis. The data are compared to published recommended values for SY-2 (Govindaraju,1984) and HPIC values following HF/$HClO_4$ acid dissolution of ALR33G and TDC-77. (R.V. - Recommended Value)

	SY-2		ALR33G		TDC-77	
	R.V.	Li-borate	HF/$HClO_4$	Li-borate	HF/$HClO_4$	Li-borate
La	75	70.9	52.3	53.5	57.1	57.2
Ce	175	164	100	103	116	115
Pr	18.8	21.6	12.9	13.3	13.6	13.9
Nd	73	79.0	48.0	49.6	56.1	53.4
Sm	16.1	16.2	9.89	9.95	10.6	12.8
Eu	2.42	2.13	3.10	3.26	3.07	2.94
Gd	17	16.0	8.22	8.37	7.92	7.93
Tb	2.5	2.13	1.09	1.10	0.98	0.99
Dy	18	14.6	5.71	5.80	5.67	5.50
Er	12.4	14.0	2.26	2.29	2.55	2.42
Yb	17	16.8	1.40	1.37	1.58	1.49

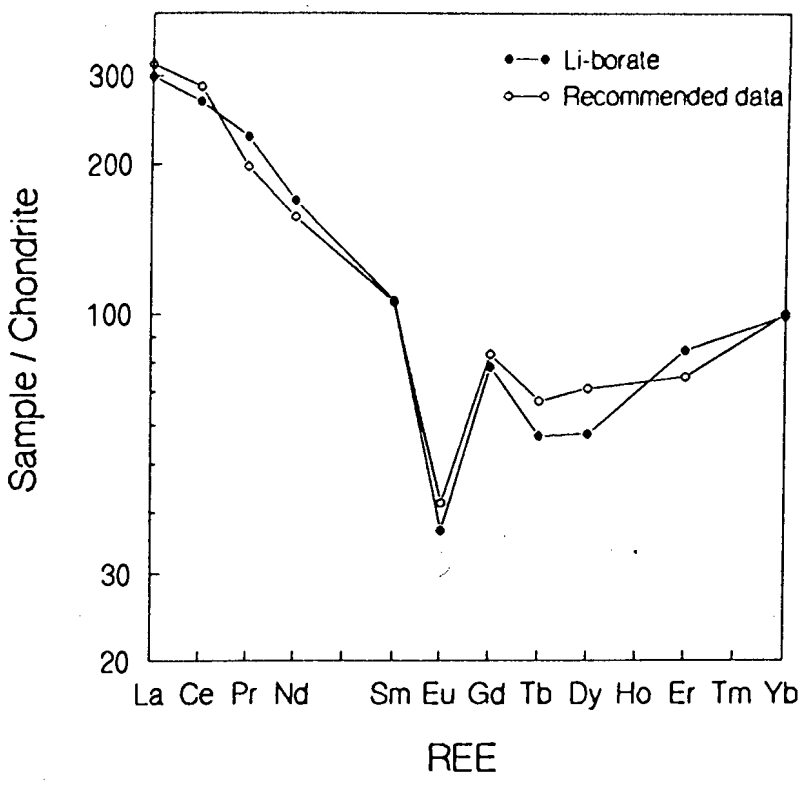


Figure 8.1: REE abundances determined by HPIC analysis and recommended values for SY-2, normalised to chondrite values.

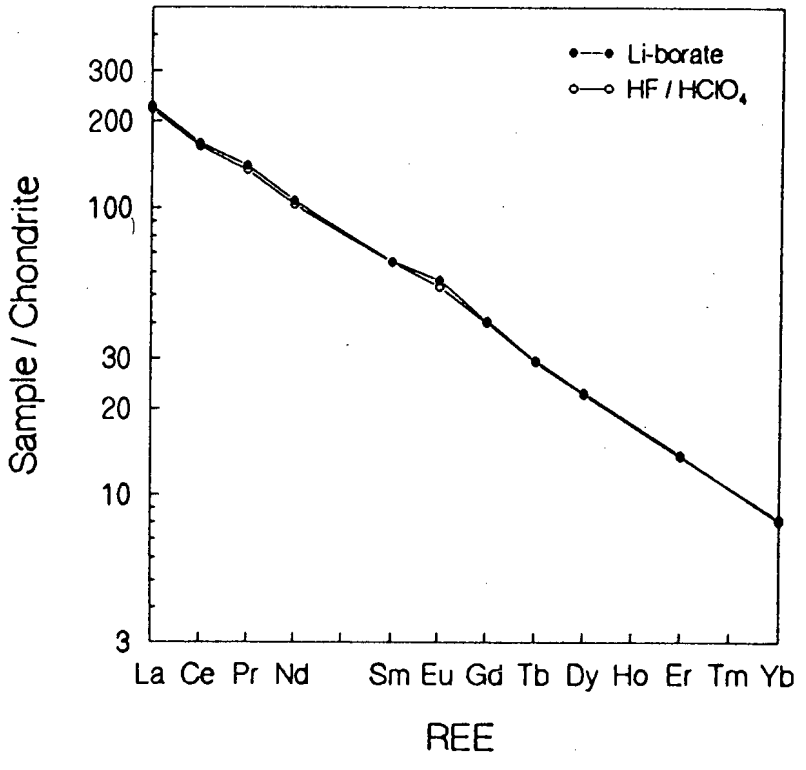


Figure 8.2: REE abundances determined by HPIC analysis of ALR33G, for both Li-borate and $HF/HClO_4$ dissolution, normalised to chondrite values.

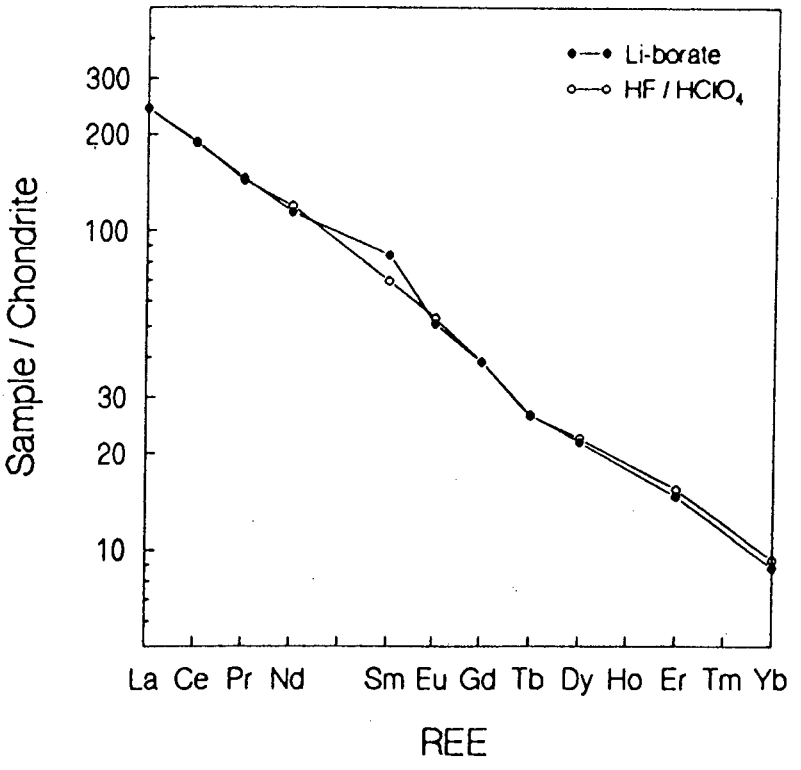
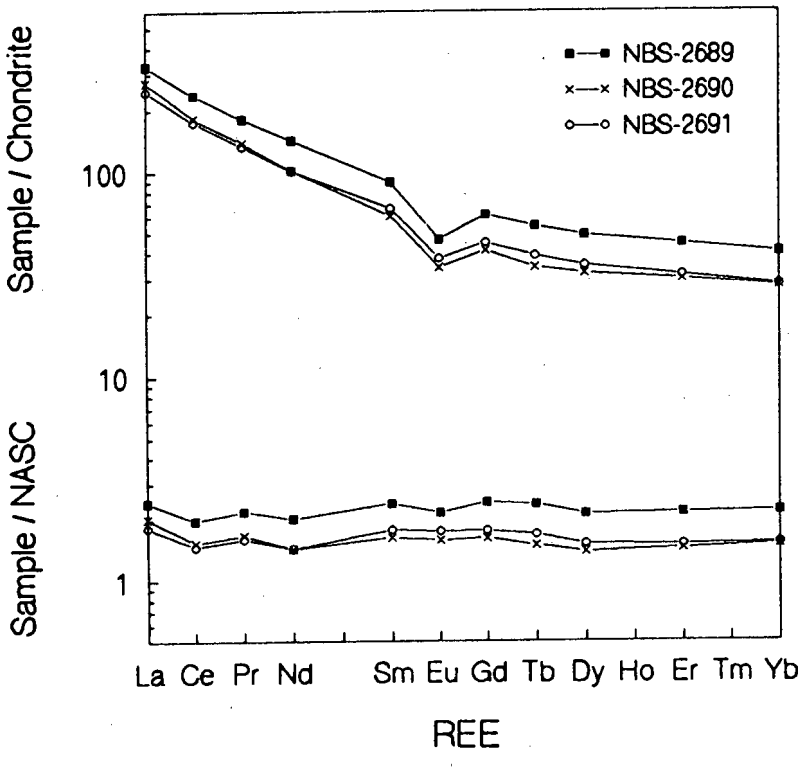


Figure 8.3: REE abundances determined by HPIC analysis of TDC-77, prepared by Li-borate and $HF/HClO_4$ dissolution, normalised to chondrite values.

Table 8.3: REE concentrations (in ppm) by HPIC analysis of fly ashes NBS-2689, NBS-2690 and NBS-2691.

	NBS-2689	NBS-2690	NBS-2691
La	77.9	64.9	58.6
Ce	145	112	107
Pr	17.3	13.2	12.7
Nd	66.8	47.6	47.5
Sm	13.6	9.29	10.1
Eu	2.69	1.96	2.18
Gd	12.6	8.38	9.20
Tb	2.02	1.27	1.44
Dy	12.4	8.03	8.78
Er	7.35	4.90	5.12
Yb	6.82	4.65	4.73

Figure 8.4: REE abundances of NBS-2689, NBS-2690 and NBS-2691, normalised to chondrite and NASC values.



8.2 ANALYSIS OF FLY ASH FROM TWO SOUTH AFRICAN POWER STATIONS

In most South African power stations a series of sequential electrostatic precipitators removes the fly ash from the flue gas before it is released into the atmosphere. The ash residue, Pulverised Fuel Ash (PFA), from coal combustion comprises 80% fly ash and 20% bottom ash. Each precipitator field removes ~70% of the ash passing through it. Therefore, the first electrostatic precipitator field removes the majority of the ash (~56%). Particle size decreases through the sequential precipitators (Bosch,1990).

The combustion process acts to concentrate a number of elements into the ash. It is well established that volatile elements such as As, Ga and Mo are volatilised at the high temperatures of coal combustion, then condense onto the surfaces of entrained fly ash particles as the temperature falls (Davidson et al.,1974, Linton et al.,1976). Similarly, it has been shown that several other volatile trace elements, such as Se, Ge and Pb, also increase in concentration with decreasing particle size, as they preferentially re-condense onto the finer particles because of the particles' greater specific surface area. Consequently, volatile trace element concentrations are found to increase with each successive precipitator field. Only S, as SO_2, is lost to the atmosphere in significant amounts (Bosch,1990).

An environmental significance of the concentrating processes is that toxic trace elements, attached to the finest ash particles, may pass through power station control devices. The finest ash remains suspended in the atmosphere for long periods, and may be inhaled by humans (Davidson et al.,1974, Linton et al.,1976).

The REE in coals are almost exclusively contained in the inorganic component. They may be concentrated within some refractory minerals. Therefore, following coal combustion the REE are concentrated in the fly ash (Bosch,1990). However, Bosch (1990) determined only La, Ce and Nd in fly ash. This study was undertaken with a view to determining the distribution of eleven of the REE in fly ash from sequential electrostatic precipitators.

Attention is more frequently being paid to utilising dumped waste products and PFA is being developed as a utilisable resource. With the increased use of REE in several industries (as

petroleum cracking catalysts, in iron and steel, in glass polishing, in colour television and in tricolour fluorescent lamps), economic interest in the REE has grown (O'Driscoll,1988). As REE are concentrated in fly ash, they may constitute a useable by-product of the ash.

8.3 SAMPLES

Samples were obtained from two South African power stations, Kendal and Lethabo, in the Transvaal. Both power stations are built adjacent to collieries. The two stations were selected as they each have seven sequential electrostatic precipitators, instead of the more usual four. The additional precipitators are designed to cope with the high ash content of the pulverised coal (~40% ash at Lethabo and 40-45% ash at Kendal) that is burnt in these power stations.

A set of samples from Kendal power station, from precipitator fields 1, 2, 3, 5 and 6 were collected by their Operations Personnel. Two sample sets were collected from Lethabo power station by Dr R. Kruger of Ash Resources, Randburg. Set 1 contains samples from precipitator fields 3 to 7, and Set 2 is a complete set of samples from all 7 fields. Approximately 750g of each sample was received from Kendal and for Lethabo Set 2. Only 100g was received for Lethabo Set 1 samples.

8.4 SAMPLE PREPARATION AND ANALYSIS

8.4.1 REE ANALYSIS BY HPIC

To homogenise the fly ash samples, after possible settling during transportation, they were mixed in a Turbula® mixer mill for ~5 minutes. The fly ash samples received from the power stations were sufficiently fine for fusing, and did not require grinding prior to sample preparation. Li-borate fusion/dissolution was used for the preparation of each fly ash sample for REE analysis. The REE were determined by direct injection of the sample solution, via a 100µl sample loop, onto the separator column. REE concentrations were resolved against a mixed REE standard solution run after every second sample. The samples were randomly prepared and analysed to avoid any trends resulting from possible instrument drift.

8.4.2 XRFS ANALYSIS

It is not usually possible to collect samples from individual electrostatic precipitator fields, and it was impossible to collect the samples in person. The samples were analysed by XRFS to determine the concentrations of some of the trace elements known to increase through the sequential precipitator fields (Willis,1987; Bosch,1990), as previous experience has shown some samples to be mis-labelled when received from power stations (Bosch,1990). Powder pellets were prepared using 8g of sample and 2g Hoechst Wax C Micropowder as binder. The samples were pressed into 30mm diameter pellets at 10 tons of pressure on ram.

8.5 DATA

The following data are presented:

1. REE concentrations by HPIC analysis, for sample sets from Kendal and Lethabo power stations are given in Tables 8.4, 8.6 and 8.8.

2. Trace element concentrations by XRFS analysis for sample sets from Kendal and Lethabo power stations are given in Tables 8.5, 8.7 and 8.9.

8.6 DISCUSSION OF RESULTS

8.6.1 XRFS ANALYSIS

Typically the more volatile trace elements analysed by XRFS (Mo, Pb, Se, As and Ge) increased sequentially through the precipitator fields (Tables 8.5, 8.7 and 8.9), showing the same trends as reported by Willis (1987) and Bosch (1990). The trace elements increased in concentration from field 1 to 6 in the Kendal power station sample set. Exceptions were fields 2 and 5, with concentrations greater than fields 3 and 6 respectively (Table 8.5). The concentrations of the volatile elements analysed, Mo, Pb, Se, As and Ge, of field 2 were significantly greater than field 3, with percentage differences between the two fields of 12% to 60%. This tends to indicate that the samples from the two fields were mis-labelled, by

Table 8.4: REE concentrations (in ppm) in fly ash from sequential precipitators from Kendal power station.

	ELECTROSTATIC PRECIPITATOR FIELDS				
	1	2	3	5	6
La	125	126	109	122	117
Ce	217	220	222	244	229
Pr	22.9	23.5	23.6	24.9	23.7
Nd	84.7	85.5	86.2	85.3	82.1
Sm	15.5	16.3	16.3	17.2	16.7
Eu	2.51	2.74	2.63	3.04	2.87
Gd	13.0	13.8	13.5	14.7	14.0
Tb	2.18	2.30	2.29	2.36	2.32
Dy	13.4	13.8	13.7	14.8	14.1
Er	7.56	7.88	7.70	8.22	7.94
Yb	7.07	7.15	7.08	7.79	7.47

Table 8.5: XRFS analysis of fly ash from sequential precipitators from Kendal power station. Trace element concentrations in ppm.

	ELECTROSTATIC PRECIPITATOR FIELDS				
	1	2	3	5	6
Mo	5	9	7	11	11
Nb	45	46	46	48	48
Zr	446	457	454	458	455
Y	84	88	87	94	95
Sr	1490	1603	1643	1796	1776
U	12	16	13	17	16
Rb	54	55	56	61	60
Th	51	55	54	61	59
Pb	55	66	58	89	84
Br	<1.1	<1.1	<1.1	<1.1	<1.1
Se	2	5	2	8	7
Bi	6	5	6	12	10
As	12	20	15	25	24
Ge	4	8	5	10	9
W	11	15	14	20	19

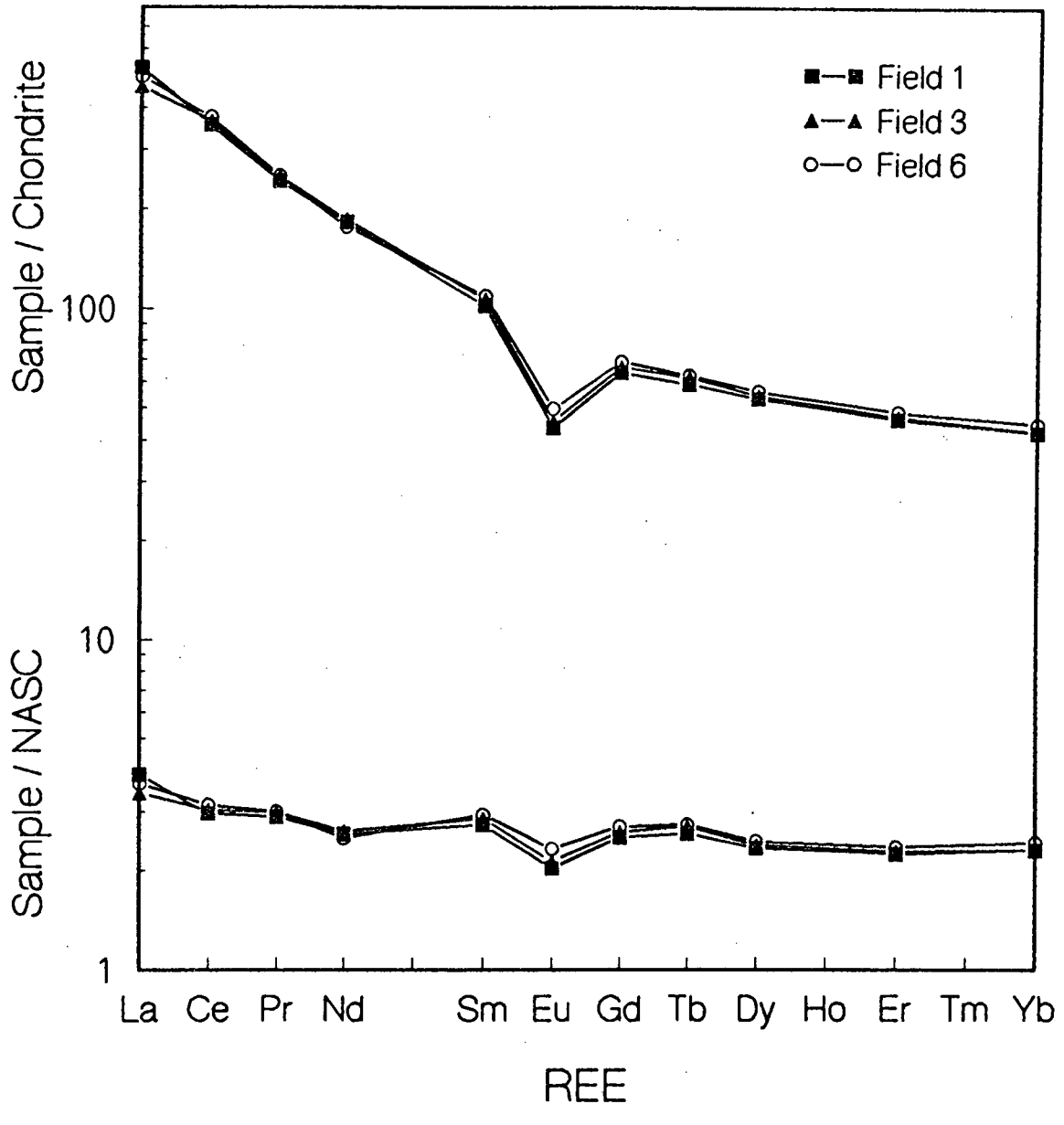


Figure 8.5: Comparison of chondrite and NASC normalised plots from electrostatic precipitator fields at Kendal power station. 2 Sigma error bars are omitted from the diagram as they are smaller than the symbols used.

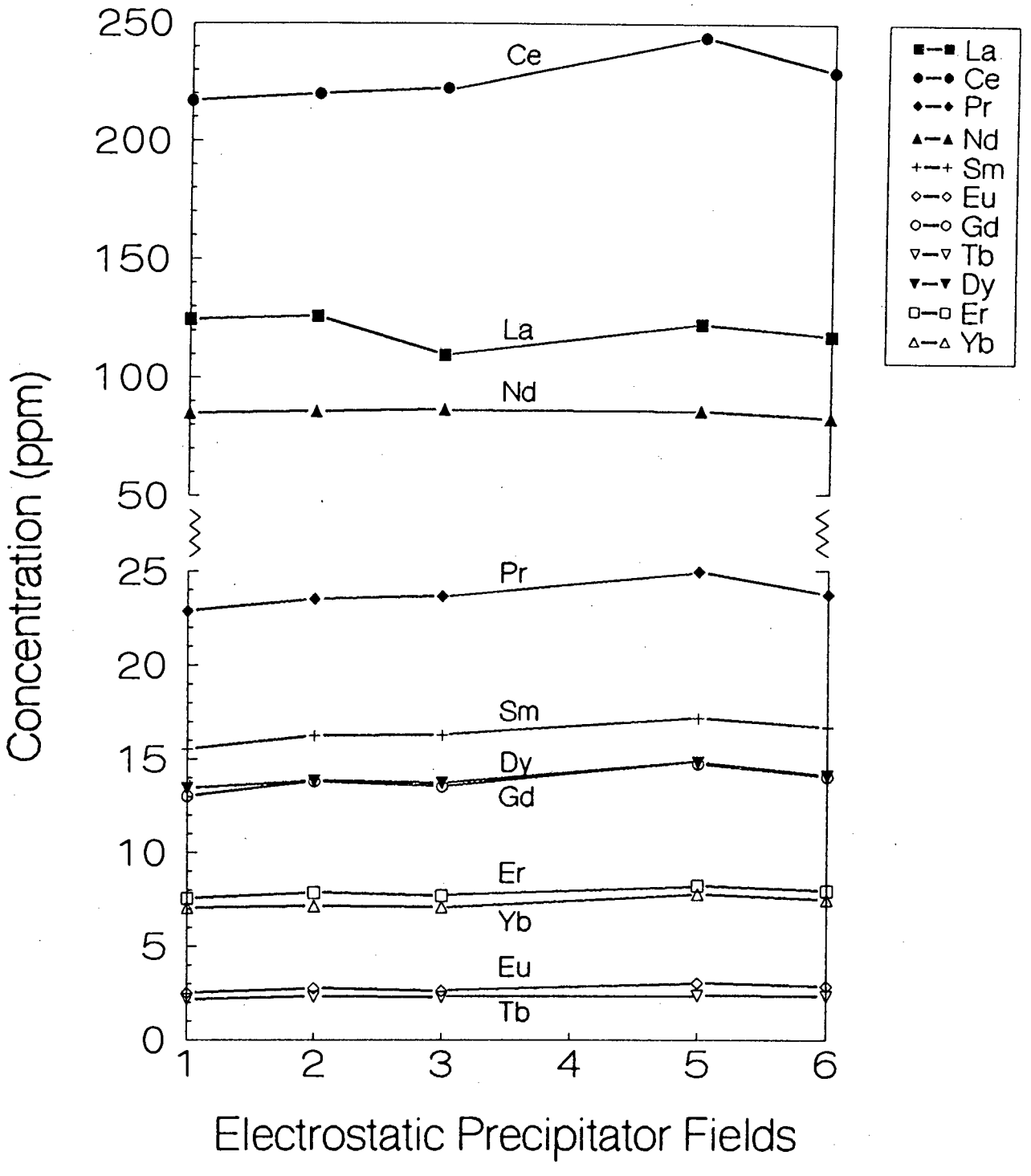


Figure 8.6: Comparison of REE abundances between sequential electrostatic precipitator fields at Kendal power station.

Table 8.6: REE concentrations (in ppm) in fly ash from sequential precipitators from Lethabo power station, set 1.

	ELECTROSTATIC PRECIPITATOR FIELDS				
	3	4	5	6	7
La	107	132	107	119	171
Ce	206	208	213	221	232
Pr	22.5	22.5	22.6	23.9	25.0
Nd	82.3	81.4	82.0	83.6	92.8
Sm	15.6	15.9	16.2	16.1	17.6
Eu	2.71	2.84	2.80	2.82	3.05
Gd	13.7	13.8	14.0	14.0	14.9
Tb	2.32	2.33	2.34	2.32	2.35
Dy	13.8	13.8	13.9	13.9	14.5
Er	7.67	7.73	7.85	7.83	7.87
Yb	7.25	7.16	7.18	7.16	7.21

Table 8.7: XRFS analysis of fly ash from sequential precipitators from Lethabo power station, set 1. Trace element concentrations in ppm.

	ELECTROSTATIC PRECIPITATOR FIELDS				
	3	4	5	6	7
Mo	2	3	5	5	6
Nb	36	38	41	43	43
Zr	402	421	410	428	423
Y	70	78	83	86	89
Sr	674	800	1028	1183	1089
U	9	11	13	13	14
Rb	35	35	39	36	39
Th	42	46	52	53	54
Pb	53	57	107	102	106
Br	<1.1	<1.1	<1.1	<1.1	<1.1
Se	2	2	14	5	7
Bi	4	<3.0	11	8	10
As	7	11	27	24	26
Ge	1	2	6	6	7
W	6	9	13	13	14

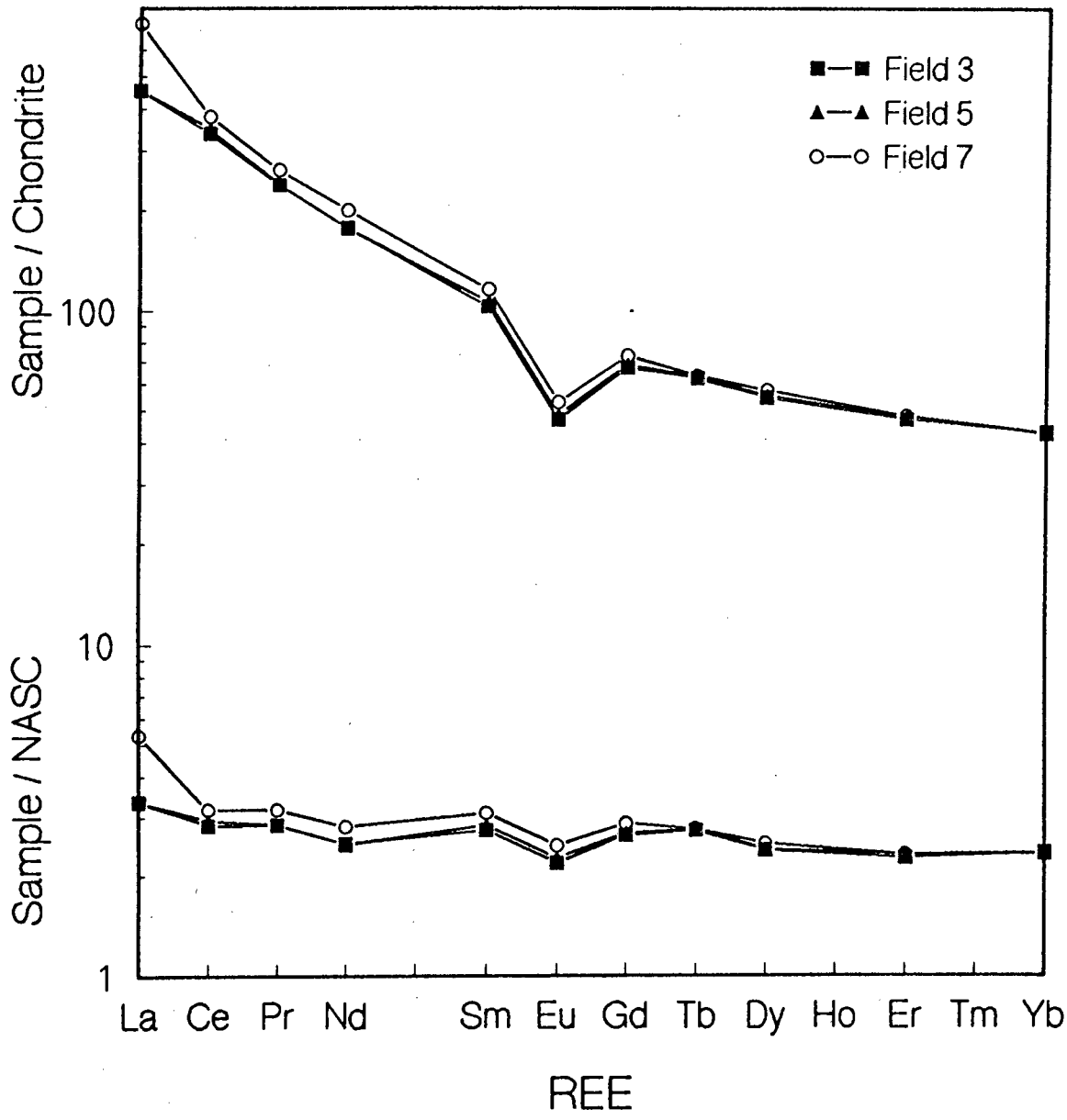


Figure 8.7: Comparison of chondrite and NASC normalised plots from electrostatic precipitator fields at Lethabo power station, set 1. 2 Sigma error bars are omitted from the diagram as they are smaller than the symbols used.

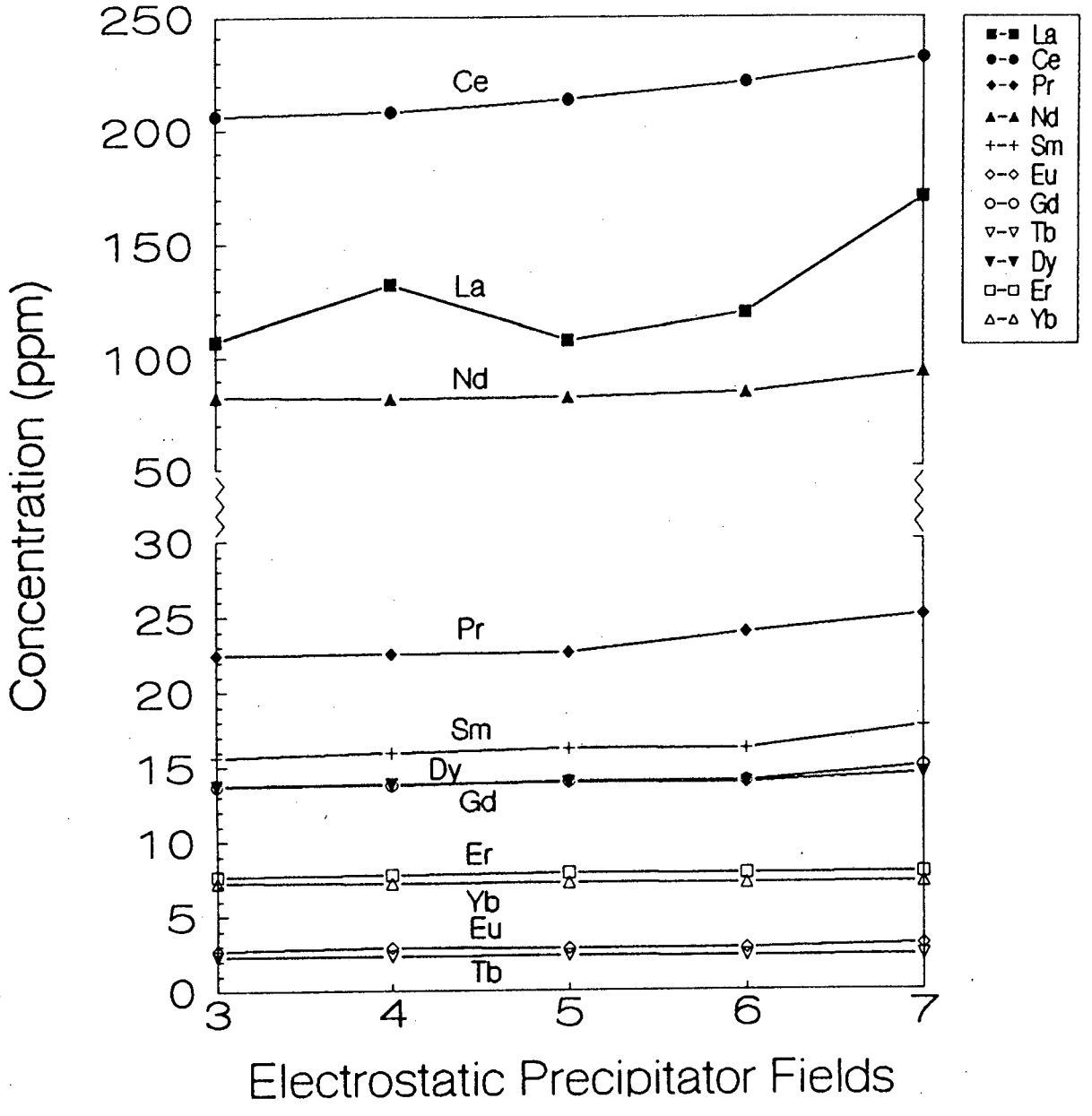


Figure 8.8: Comparison of REE abundances between sequential electrostatic precipitator fields at Lethabo power station, set 1.

Table 8.8: REE concentrations (in ppm) in fly ash from sequential precipitators from Lethabo power station, set 2.

	ELECTROSTATIC PRECIPITATOR FIELDS						
	1	2	3	4	5	6	7
La	80.6	103	102	101	108	112	111
Ce	169	185	199	199	209	217	214
Pr	18.8	19.8	21.7	21.28	22.6	23.2	23.3
Nd	67.1	71.3	79.0	77.4	81.4	82.7	85.7
Sm	13.2	13.7	15.3	15.3	15.6	16.2	16.3
Eu	2.31	2.36	2.62	2.57	2.67	2.72	2.78
Gd	11.4	11.9	13.27	13.23	13.8	14.1	14.1
Tb	1.86	1.98	2.24	2.23	2.33	2.38	2.33
Dy	11.3	11.9	13.2	13.2	14.0	14.3	14.2
Er	6.30	6.66	7.34	7.44	7.76	7.96	7.84
Yb	5.79	6.05	6.78	7.02	7.17	7.35	7.28

Table 8.9: XRFS analysis of fly ash from sequential precipitators from Lethabo power station, set 2. Trace element concentrations in ppm.

	ELECTROSTATIC PRECIPITATOR FIELDS						
	1	2	3	4	5	6	7
Mo	2	3	5	5	6	6	5
Nb	36	38	42	43	43	45	46
Zr	406	424	414	433	429	430	426
Y	71	78	84	86	89	91	94
Sr	678	804	1033	1191	1089	1161	1171
U	11	12	13	13	15	15	14
Rb	35	36	39	37	40	40	39
Th	44	46	53	53	54	56	59
Pb	52	59	109	101	106	121	145
Br	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1
Se	1	2	14	5	8	8	9
Bi	<3.0	6	8	8	13	15	13
As	7	10	26	25	26	26	25
Ge	<0.9	2	6	5	6	7	7
W	5	9	13	15	13	14	11

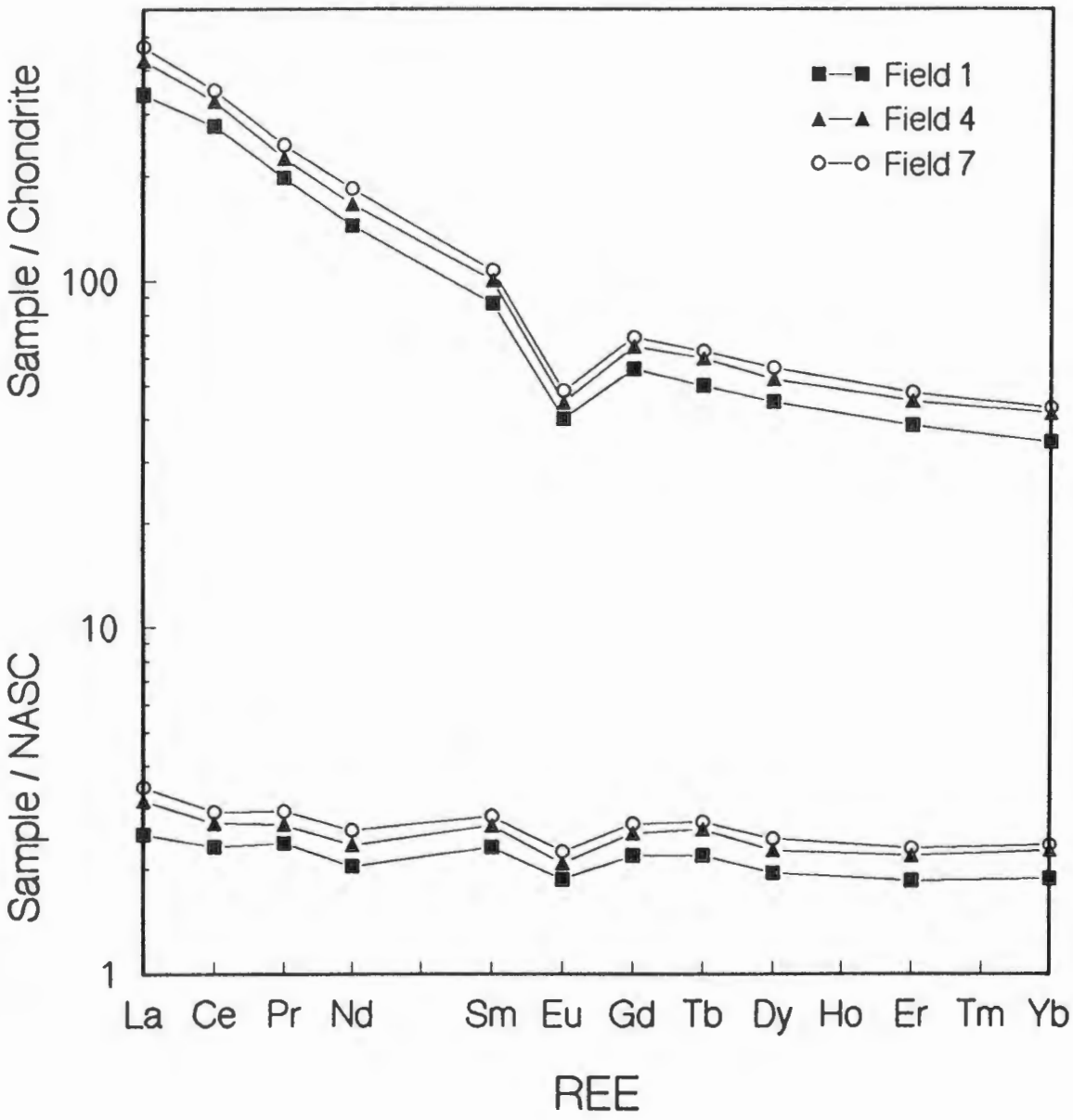


Figure 8.9: Comparison of chondrite and NASC normalised plots from electrostatic precipitator fields at Lethabo power station, set 2. 2 Sigma error bars are omitted from the diagram as they are smaller than the symbols used.

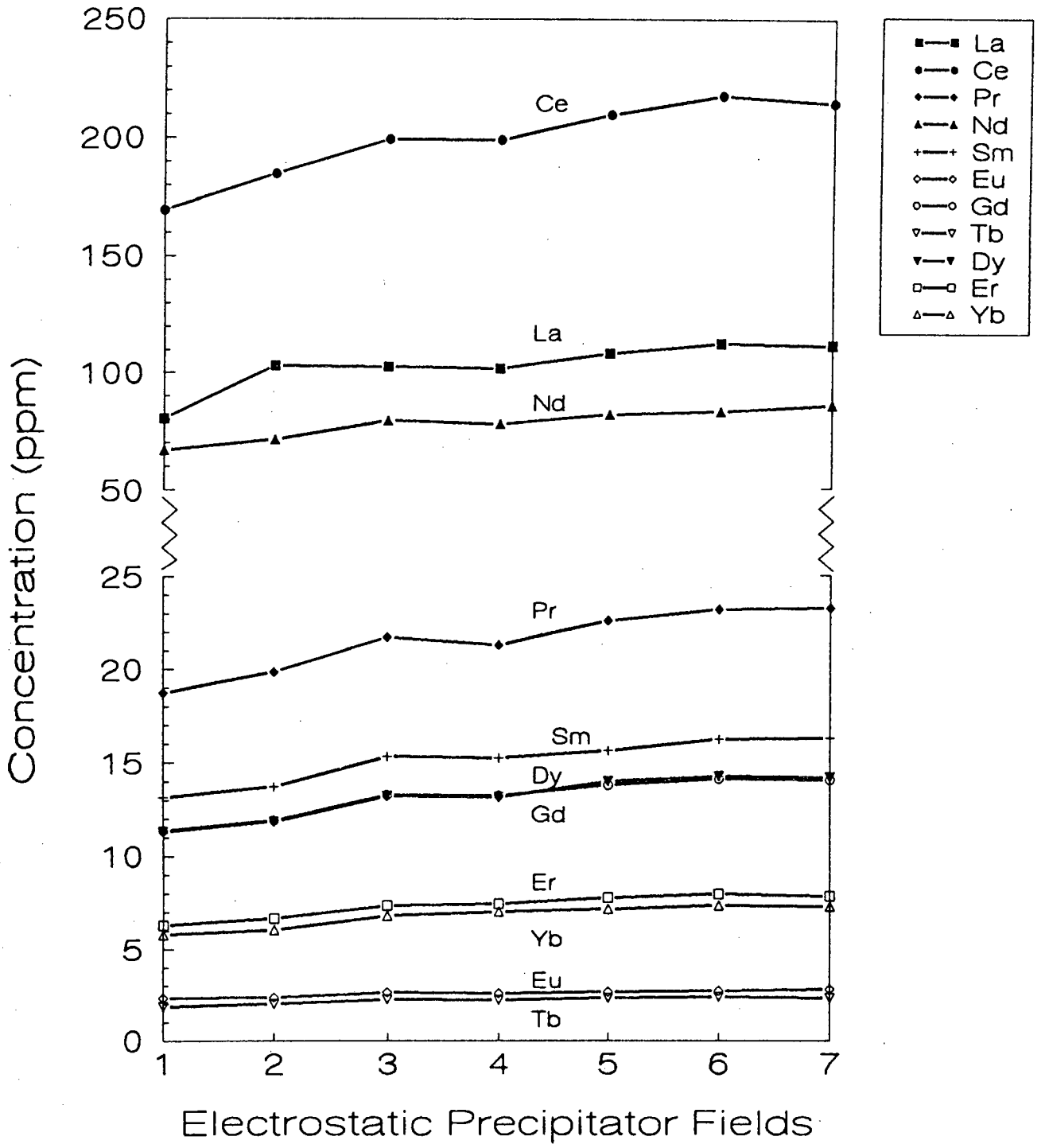


Figure 8.10: Comparison of REE abundances between sequential electrostatic precipitator fields at Lethabo power station, set 2.

Kendal personnel. The differences observed between fields 5 and 6 were less significant, therefore, it must be assumed that the samples were correctly labelled. Samples could not be recollected. The collection of fly ash samples requires access to the precipitator, which requires shut down of the precipitator.

XRFS data of sample sets 1 (fields 3 to 7) and 2 (fields 1 to 7), from Lethabo power station, show increasing concentrations for the elements analysed (Tables 8.7 and 8.9). The concentrations of Pb, Se and As in field 5, set 1, were greater than their concentrations in field 7. The concentrations of Pb and Se in field 3, set 2, are significantly higher than their concentrations in field 4. The increase in the volatile elements through the precipitator fields results from the preferential re-condensing of the volatile elements onto finer particles (section 8.6.3)

8.6.2 REE ANALYSIS

Typically the REE analyses showed increasing REE concentrations from precipitator field 1 to field 7 at Lethabo power station and fields 1 to 6 at Kendal power station (Tables 8.4, 8.6 and 8.8). The percent difference between adjacent precipitators was usually less than 5%. However, the REE concentrations increased systematically from field 1 to 7. The overall increase from field 1 to 7 was typically greater than 5%.

The REE data of Kendal power station increased from field 1 to 6 (Table 8.4, Figs. 8.5 and 8.6), but like the XRFS data, concentration levels in field 2 were greater than field 3. Similarly field 5 values were higher than field 6, although the percent difference was within analytical error. Variable La values were recorded and no trends were evident for Nd concentrations. The mean percent increase for REE from fields 1 to 5 (Field 5's concentrations were typically higher than field 6), excluding La, was 9%, ranging from 7% (Tb) to 11% (Ce). The slope of chondrite and NASC normalised patterns were approximately constant for each precipitator field (Fig.8.5), so indicating a proportional increase in concentration for each REE between precipitator fields.

The REE data of Lethabo set 1 increases from field 3 to 7 (Table 8.6, Figs. 8.7 and 8.8). La values are variable, possibly due to the contamination sources discussed previously (section 7.4.1). Nd values decrease from field 3 to 4 then increase from field 4 to 7 (Fig.8.8). The heavy REE, Tb to Yb, show less than 5% increase from field 3 to 7. The consistent concentration of these elements may be seen in Figure 8.8. The greatest difference between two fields was observed between fields 6 and 7; where the percent increase was typically greater than 5%. The mean increase for REE Ce to Gd, across the fields analysed was 11% (8% Gd - 12% Sm).

REE data for Lethabo set 2 show a continual increase from field 1 to 7 (Table 8.8, Figs. 8.9 and 8.10). There are slight variations between fields 3 and 4, but concentration differences between the two fields are less than 5% (Fig.8.10). A mean increase from fields 1 to 7 for all REE is 21% (17% Eu - 27% La). The linear increase between fields is apparent on the chondrite and NASC plots (Fig.8.9) as the plots remained parallel although the concentration between fields increased. The most significant increase in REE concentration occurs from fields 1 to 3 (Fig.8.10) with only slight increases occurring from fields 4 to 7.

8.6.3 POSSIBLE CAUSES FOR THE INCREASE IN REE CONCENTRATION

Mineralogical changes recorded by Bosch (1990) in fly ash from Lethabo power station show that quartz, believed to be from the original coal, decreased across the precipitator fields, as the large grains were preferentially extracted by the first few precipitators. Typically the content of glass and other minerals, e.g. mullite (derived from kaolinite in the original coal) and spinels, increased in concentration across the precipitator fields. Therefore, the REE would be expected to increase as the diluting effect of quartz on the glass and other minerals present in fly ash is reduced through the sequential precipitators.

Grain size of the fly ash from Lethabo was found to decrease from precipitator fields 1 to 4 and then remain constant to field 7 (Bosch,1990). Several trace elements are known to preferentially re-condense onto finer particles, so becoming concentrated through the precipitator fields. However, it is unlikely that the increase in REE concentration was similarly influenced, as REE bearing minerals, e.g. zircon, in the fly ash would have been

derived from the original coal and would not have undergone volatilization during the combustion process. The REE are typically volatilized only at temperatures in excess of 2000°C (Weast,1975).

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

9.1 CONCLUSIONS

A gradient HPIC analytical technique was successfully developed for the generation of high quality REE data for coal, including low ash (low REE) varieties, and fly ash. The technique comprised two stages. A preliminary bulk separation of the REE from the sample matrix by cation exchange was required. The technique, allowed for the routine determination of all naturally occurring REE, except Ho and Lu, by anion exchange separation using combinations of various chelating agents.

As samples must be in solution for analysis by gradient HPIC, experiments were carried out to determine the most suitable methods for dissolving coals and fly ash. REE frequently occur in considerable concentration in resistant minerals. Therefore, complete sample dissolution had to be assured.

Microwave digestion proved to be a practical means for the effective dissolution of whole coals. A two stage digestion procedure removed the necessity of ashing. Consequently, the application of microwave digestion is advantageous where a large number of coal samples are to be analysed on a routine basis, as time saving is considerable and the use of closed, pressurized vessels provides little risk of contamination. However, the pressure limits of the digestion vessels restricts the amount of sample which may be dissolved. During the present study, two 0.1g aliquots of each sample were combined after microwave digestion, to give a sample size of 0.2g. The use of higher pressure digestion vessels than were available for the present study should ensure a more satisfactory sample size of ~0.5g.

Sample solutions of coal were prepared by conventional ashing procedures to ascertain the effectiveness of the microwave dissolution procedure. Two procedures, which differed in

their ashing rate, were evaluated. Ashing is time consuming for routine analysis of coals and contamination and sample loss may occur.

The complete dissolution of fly ash was successfully achieved by fusing with lithium metaborate/tetraborate flux, a powerful flux which attacks resistant minerals, then dissolving the fusion "bead" in dilute HCl. Alternative dissolution procedures of $HF/HClO_4$ dissolution and microwave digestion proved incapable of providing a complete dissolution.

Prior to REE determination by HPIC analysis the bulk of the sample matrix had to be removed, as the transition metals behave similarly to the REE under the analytical conditions used in this study. Bulk separation of the REE from the transition metals and most other matrix components was successfully achieved by cation exchange separation. Modification of the separation procedure, to enable savings in time and acid quantities used, was limited by the need to provide adequate separation of a great variety of coal and fly ash compositions.

HPIC detection limits, using direct sample injection via a 100µl sample loop, are typically in the ppb range (10-100ppb). However, REE concentrations in low ash coals, prepared by microwave digestion, were insufficient to enable satisfactory detection by this means. Therefore, on-line sample concentration was employed. The concentration procedure allowed for the analysis of several *millilitres* of sample solution, rather than the usual 100µl, thus providing adequate detection limits for coals with as little ash as 6% (1-10ppb of individual REE). Small differences in the acid concentrations, between samples and standards, affected the degree of swelling of the concentrator column resin and, therefore, the volume of sample solution passing through the concentration column in a given time. To ensure that a precise volume of sample passed though the concentrator column, the sample solution exiting the column was measured by means of a plastic, non-wetting measuring cylinder. Precisions of <5%CoV, for most REE, were recorded for the on-line concentration procedure.

Gradient ion chromatography may be used to separate the REE as either anionic or cationic complexes. The elution order of REE following cation separation is Lu to La. For this reason, normally cation separation would be favoured for the analysis of coal and fly ash samples, as the least abundant REE are eluted early when peaks are sharper and sensitivity

is higher. However, severe matrix problems were experienced when developing the technique. Low concentrations (ppb) of matrix elements, remaining in the sample solution despite off-line matrix separation, coeluted with the REE, precluding accurate REE determination. Cation exchange separation was, therefore, eliminated as a feasible method for REE determination of coal and fly ash. However, if "clean" samples could be obtained the technique would provide a valuable complementary method to anion exchange.

Anion separation of the REE, with an elution order of La to Lu, was successfully applied to coal and fly ash. Only Ho, which coelutes with the more abundant Y, and Lu, which is inadequately resolved from Yb, could not be determined.

Transition metals, remaining in the sample solution after off-line matrix separation, were removed from the separator column by Pyridine-2,6dicarboxylic acid (PDCA) prior to the removal of the REE by oxalic and diglycolic acid. Precise eluent chemistry is required to ensure accurate REE determination. The consequence of variations in eluent composition was clearly illustrated by the problem encountered with the splitting of the Nd peak. An unidentified contaminant in the PDCA eluent resulted in a two-fold elution of Nd. The problem was overcome only by using a high purity PDCA (Dionex® PDCA). Eluent gradients provide a means of producing maximum possible peak separation in the complex REE chromatogram. However, a drawback of "gradients" is the inevitable change in baseline as eluent composition varies. Modifications to the gradient programme used during this study can provide sufficient resolution of the Yb and Lu peaks to enable the determination of Lu, should this be required. Modifications tested, however, had the effect of reducing the quality of the remainder of the chromatogram.

The accuracy and precision of the HPIC anion separation technique for the determination of REE in coal samples, following microwave digestion, was established by repeated analysis of international standard reference materials (SRMs). The precision for each element was typically <5%CoV in spite of the small 0.2g sample size. The precision of Tm was poorer, as the concentrations of this element were close to the lower limit of detection. The technique's accuracy was gauged by the coherency and smoothness of plots when the REE data were normalised to chondrite and NASC values. REE values of SRMs determined by

HPIC compared closely with available published data. Frequently, normalised HPIC REE data from this study produced smoother plots on chondrite normalised diagrams than previous published values, suggesting that the HPIC data was more accurate.

The HPIC technique was applied to the determination of REE concentrations in a new reference coal sample, USGS CLB-1. Reproducibility for each REE was <5%CoV, with the exception of Eu. The poorer Eu reproducibility is considered to have resulted from an inhomogeneity in one of the three bottles of sample provided. X-Ray Fluorescence Spectrometry (XRFS) data indicate the possible presence of additional quantities of plagioclase in this bottle, which would account for anomalously high Eu values. The data show a high degree of coherency when normalised to chondrite and NASC values. Good agreement was found between the HPIC data, from this study, and the provisional REE values provided by Dr. J.Kane.

HPIC REE data of ashed coal samples typically produced low light REE values relative to those determined following microwave digestion. A greater decrease in light REE concentrations was observed for the fast ashing procedure relative to the slow ashing procedure. X-Ray Diffraction analysis showed no mineralogical differences between the ash produced by the two ashing procedures. Zn, Cu, Ni and Ga were determined by XRFS analysis for ash from both ashing procedures. The Ni value remained constant, relative to the recommended value, during ashing. Cu and Ga decreased and Zn increased in concentration (for two of the samples analysed) during the ashing procedures.

It is considered that as REE are only volatilized at temperatures in excess of 2000°C they could not have been lost due to vaporization. REE may have been liberated if some light REE enriched mineral, e.g. clay minerals or phosphates, in the coal was broken down during ashing. REE may then have been lost with particulate matter during smoke production.

Reproducibility of the HPIC analytical technique for REE determination following Li-borate fusion of fly ash was <6%CoV. Accuracy was gauged from the determination of REE in silicate rock samples with REE concentrations similar to fly ash, as no SRM values for fly

ash were available. HPIC REE values for the rock samples compared well with recommended values.

The distribution of REE in fly ash from sequential electrostatic precipitators at Kendal power station and two sets of samples from Lethabo power station were determined. REE concentrations increased systematically from the first precipitator field to the last (fields 1 to 7). The overall increase was generally greater than the relative error of 5%. The quantity of quartz decreased through the precipitators. The increase in REE concentration is probably related to the reduction of the diluting effects of quartz on the glass and other minerals in fly ash.

Gradient HPIC analysis provides an effective means for the routine determination of REE in coals and fly ash. The technique described compares favourably with alternative techniques (e.g. INAA and ICP-AES) for routine REE analysis in terms of limits of detection, accuracy and precision.

An advantage of HPIC lies in the low capital and running costs. The technique has great potential over INAA which has the disadvantage of requiring access to a nuclear reactor. HPIC is easy to operate, but care is required over sample and eluent preparation and experience is needed in the evaluation of chromatograms, in order to obtain accurate and precise data. In addition to REE analysis of coals and fly ashes the analytical technique can easily be adapted for the determination of other elements.

9.2 RECOMMENDATIONS

The use of higher pressure digestion vessels (e.g. HPV 80®, Milestone) than were available during the present study should enable a larger sample size (~0.5g) to be used for analysis of REE in coal. The digestion programme used during the present study should be optimised for the simultaneous irradiation of up to 8 pressure vessels. Further work is required on the microwave digestion of fly ash. Microwave dissolution of fly ash would enable rapid digestion and limit risks of contamination, particularly in laboratories where lanthanum-bearing fluxes are routinely used.

The causes of the loss of light REE when ashing coal samples, and the variation in loss of elements under different ashing conditions, have important implications in trace element analysis of coals using ashing procedures and require further investigation. A study to determine the distribution of REE between the different components of coal, i.e. whether REE are present within the organic fraction, is recommended. It would be of interest to determine whether other trace elements behave similarly to the REE during ashing. The loss of light REE during the ashing process calls into question results obtained by this means of sample preparation.

If at all possible, fly ash samples should be collected by the researcher, to prevent sample mis-labelling. A future study of the behaviour of REE following combustion of coal should, for completeness, also include bottom ash samples and samples of the original coal.

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APPENDIX 1

Plumbing configuration of (a) the injection valve, for both direct injection and on-line sample concentration, and (b) the column select valve. On all Dionex® injection and column select valves the ports are numbered sequentially from port 1, above the ventilation hole, clockwise to port 4, then from port 5, below the ventilation hole, clockwise to port 8.

a)

PORTS	DIRECT INJECTION	PRE-CONCENTRATION
1	To pump - eluent in	To pump - eluent in
2	To by-pass loop	To by-pass loop
3	Sample inlet	To waste (record outflow)
4	Sample loop	To concentrator column
5	To port 1 of column select valve	To port 1 of column select valve
6	From by-pass loop	From by-pass loop
7	Sample syringe	From auxiliary pump
8	Sample loop	From concentrator column

b)

PORTS	LINE
1	Eluent in from Port 5 of injection valve
2	To anion guard column
3	Blocked
4	To cation guard column
5	To conductivity cell
6	To suppressor
7	Blocked
8	From cation separator column

APPENDIX 2

Experimentation to determine the optimal microwave digestion procedure for (a) coal and (b) fly ash samples.

a)

TRIAL	WEIGHT (g)	STEP	REAGENT	VOLUME (ml)	POWER (%)	TIME (min)	PERCENTAGE DISSOLVED
1	0.150	1	HNO_3	5	25 50	5 0.5	50
		2	HF	5	25 50	7 1	
2	0.150	1	HNO_3 H_2O_2	4 1	25 50	7 1	40
3	0.150	1	HNO_3	3	25 50	9 1	55
4	0.150	1	HNO_3	3	25 50	7.5 1.5	70
		2	HF	5	25 50	7 0.75	
5	0.150	1	HNO_3	3	25 50	7.25 1.75	75
		2	EVAP.		30	3	
		3	HF	5	25 50	7 1.25	
6	0.150	1	HNO_3	4	25 50	7 2	75
		2	EVAP.		20	3	
		3	HF	6	25 50	6 1.5	
7	0.150	1	HNO_3	3	25 35 50	6 1 1.5	70
		2	EVAP.		20	4	
		3	HF	5	25 35 50	6 1 1	
8	0.150	1	HNO_3	3	25 50	10 3	80
		2	EVAP.		20	4	
		3	HF	5	25 50	8 1	

9	0.150	1	HNO_3	3	25	8	95
					50	3	
		2	EVAP.		20	4	
		3	HF	5	25	8	
			H_2O_2	0.5	50	1	
10	0.150	1	HNO_3	3	25	9	100
					50	3	
		2	EVAP.		20	4	
		3	HF	5	25	8	
			H_2O_2	1	50	2	
11	0.100	1	HNO_3	3	25	4	97
					50	2	
		2			25	4	
					50	2	
		3	EVAP.		20	8	
		4	HF	4	25	5	
					50	2	
12	0.100	1	HNO_3	3	25	4	98
					50	2	
		2	HNO_3	1	25	4	
					50	2	
		3	EVAP.		20	9	
		4	HF	4	25	5	
					50	3	
13	0.100	1	HNO_3	2	25	3	98
			H_2O_2	1	50	4	
		2	HNO_3	1	25	3	
					50	4	
		3	EVAP.		20	8.5	
		4	HF	4	25	3	
			H_2O_2	1	50	4	
14	0.100	1	HNO_3	3	25	3	100
					50	4	
		2	H_2O_2	1	25	3	
					50	4	
		3	EVAP.		20	6	
		4	HF	4	25	3	
					50	4	

PERCENTAGE DISSOLVED - Estimated percentage, by observation, of the sample which dissolved during the digestion procedure.

EVAP. - Open evaporation

b)

TRIAL	STEP	REAGENT	VOLUME (ml)	POWER (%)	TIME (min)	PERCENTAGE DISSOLVED
1	1	HF HCl HNO_3	6 2.25 0.75	25 30	2 7	70
2	1	HF A.R.	7 2	25 30	2 7	70
3	1	HF HCl HNO_3	7 1 1	25 30	2 7.5	70
4	1	HCl HNO_3 $HFBO_3$	1 1 7	25 30	2 7	65
5	1	HNO_3 HF	3 6	25 30	2 7	70
6	1 2	HNO_3 HF $HClO_4$	2 5 1.5	25 30 25 30	2 8 2 4	75
7	1 2 3	HNO_3 EVAP. HF	3 4	25 50 20 25 30 50	5 1 4 - 6 5 1 1	68
8	1 2	HNO_3 HF EVAP.	3 3	25 50 20	3 4 12	50
9	1	HNO_3 HF	3 1.5	25 50	3 4	80
10	1 2 3	HNO_3 EVAP. HNO_3 HF H_2O_2	2 1 3 0.5	25 50 20 25 50	3 2 8 3 4	78
11	1	HNO_3 HF	4 2	25 35 50	4 2 2	80
12	1	HNO_3 HF	2 4	25 35 50	4 2 2	82

A.R. - Aqua Regia

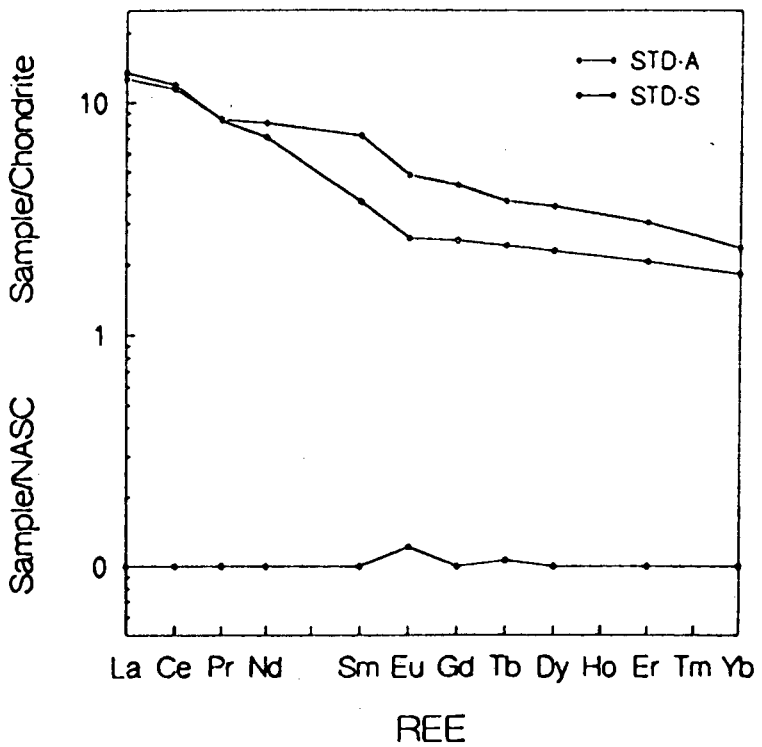
APPENDIX 3

(a) REE values of Chondrite (Sun & McDonough, 1989), North American Shale Composite (NASC) (McLennan,1989), and standard solutions A and S (in ppm). (b) Chondrite normalised REE plots of Std-A and -S, and NASC normalised REE plot of Std-S.

a)

	CHONDRITE	NASC	STD-A	STD-S
La	0.237	32	3.00	3.20
Ce	0.612	73	7.00	7.30
Pr	0.095	7.9	0.80	0.79
Nd	0.467	33	3.80	3.30
Sm	0.153	5.7	1.10	0.57
Eu	0.058	1.24	0.28	0.15
Gd	0.206	5.2	0.90	0.52
Tb	0.037	0.85	0.14	0.09
Dy	0.245	5.8	0.90	0.58
Er	0.166	3.4	0.50	0.34
Tm	0.025	0.50	0.06	0.05
Yb	0.170	3.1	0.40	0.31

b)



APPENDIX 4

Manuscript accepted for publication and presented at the 2nd International Conference on Elemental Analysis of Coal and its By-Products, Kentucky, U.S.A (September 1991).

RIDLEY, M.K., WATKINS, R.T. and WILLIS, J.P. Determination of Rare Earth Elements in Whole Coal and Fly Ash by Gradient Ion Chromatography.

DETERMINATION OF RARE EARTH ELEMENTS IN WHOLE COAL AND PULVERIZED FUEL ASH BY GRADIENT ION CHROMATOGRAPHY

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ABSTRACT

High performance gradient ion chromatography (HPIC) employed in the Department of Geology, University of Cape Town, enables the routine determination of up to 12 rare earth elements (REE) in coal and pulverized fuel ash by anion separation. The use of on-line sample concentration gives detection limits of ~10 ppb in the original solid sample. Such detection limits are satisfactory even for the analysis of low-ash coals and allow the use of microwave digestion of coal samples in which sample size is limited. A lithium metaborate/lithium tetraborate fusion technique is used for the dissolution of pulverized fuel ash and coal ash. Results for international low ash coal reference materials NBS-1632a, SARM-18, and USGS CLB-1 and fly ash reference materials NBS-2689, NBS-2690 and NBS-2691 show a reproducibility generally <5% CoV for each of the REE. The results from these materials and high ash coal reference materials SARM-19 and SARM-20 generally compare closely with those produced by INAA and fall within the ranges of published values. Highly coherent chondrite-normalised REE patterns plotted from the results, and flat patterns produced when the measured REE concentrations are normalised to a "shale composite", provide further indication of the accuracy of the data produced by the technique. Concentrations of light REE obtained for three *ashed* coal CRMs are lower than those obtained using the microwave digestion technique, although the heavier REE are similar for both methods of preparation. The HPIC method provides a convenient, low cost alternative to ICP-AES, ICP-MS, ID-MS and INAA for the analysis of rare earth elements. The method is suitable for routine application to coal and its by-products.

INTRODUCTION

High performance ion chromatography (HPIC) is an effective technique for

determining the rare earth elements (REE) in geological materials. A method in which the REE are separated as anionic complexes is employed in the Department of Geology, University of Cape Town, in the routine determination of REE in silicate rocks[1] . Recently, this facility has been extended to the determination of REE in coal and pulverized fuel ash[2].

As in other "wet chemical" analytical techniques, HPIC requires the sample to be in solution. For coal, this is achieved by the use of microwave digestion, which removes the necessity of ashing and is consequently more rapid. The use of closed high-purity PTFE pressure vessels minimises the risk of sample loss and contamination. Contamination may be an especially important factor in busy laboratories where many samples are prepared simultaneously, and is to be particularly guarded against where XRF techniques using lanthanum-bearing fluxes are employed. Samples of pulverized fuel ash, which frequently contain highly resistant spinel, are taken into solution by fusing with lithium metaborate/lithium tetraborate.

In the HPIC analysis, solutions of pulverized fuel ash, which mostly contain concentrations of REE similar to those of silicate rocks, may be directly injected onto the separator column by means of a sample loop. A method of on-line sample concentration, whereby the volume of solution analysed is increased as much as 100x, provides adequate detection limits for coals, including low ash varieties containing much reduced REE concentrations, and overcomes the limitations of sample size presently imposed by the microwave dissolution technique.

The method of anion separation by gradient elution employed in our laboratory enables the routine determination of all naturally occurring REE except Ho and Lu. The sample dissolution techniques and HPIC analytical procedures are described in this paper and their advantages and disadvantages discussed. REE data obtained from a recent programme of analysis of international coal and fly ash reference materials will be reviewed. The results of a programme of analysis to determine the REE content of the new

low ash coal standard USGS CLB-1 (Watkins *et al. in prep.*[3]) will also be presented.

The present methods are subject to improvement, particularly with regard to an increase in sample size. Nevertheless, they have proved successful in providing high quality REE analyses on a routine basis.

ANALYTICAL PROCEDURES

Sample Dissolution

Coal Traditionally, the dissolution of coal has been preceded by the time consuming process of ashing to remove the organic matter. Microwave radiation has been successfully applied to the dissolution of organic materials, such as plants and meats[4][5][6]. When microwaves are applied to a sample in a closed vessel, temperature rise is rapid and high temperatures and pressures are attained, decreasing the acid:sample ratio required for dissolution. However, care must be taken not to exceed the pressure limit of the vessel as this may lead to vapour leakage and sample loss or, more seriously, rupture of the vessel. Particularly high pressures are produced during coal dissolution on account of the very high content of organic matter. In the present study, medium pressure vessels, rated to 80bars, were used limiting the amount of powdered coal that could be dissolved to 0.1g.

An MLS 1200 microwave system, manufactured by Milestone GmbH, Leutkirch, Germany[7] was used. The system incorporated a 1200 watt oven with power settings which could be varied in 1% increments. Integral microprocessor control and programming increased the reproducibility of dissolution routines. The digestion vessels were constructed of PTFE and encased in protective polypropylene shields.

0.1g of finely powdered, homogenised coal was weighed into the pressure vessel and 3ml of 14M HNO_3 were added. The vessel was closed, hand torqued, and irradiated for 3 minutes at 25% power and then 4 minutes at 50% power. 2 vessels were irradiated

simultaneously on a rotating carousel and were then cooled for 15 minutes in a water bath. 1ml of 32% H_2O_2 was added to the sample and the two stage irradiation repeated. This procedure effectively removed all organic components from the coal. The resulting solution was evaporated to near dryness by applying 20% power to the open vessels for ~6 minutes. Complete drying was avoided as this gave rise to insoluble residues. 4ml of 28M HF were then added and the two stage irradiation repeated once more to effect the dissolution of the inorganic coal constituents.

In routine coal analysis, 2 aliquots of each sample (0.2g coal in total) were combined after microwave dissolution and the combined solution evaporated to dryness. 10ml of 4M HCl was used to dissolve the dried combined sample, which was then diluted to 75ml with distilled water. If no undissolved matter was visible, the solution was further diluted to 100ml. With some coals a small amount of resistant inorganic material may remain after the microwave treatment. This was experienced in the present study only in the case of USGS CLB-1.

Residual inorganic mineral grains were subjected to a "mini-fusion" with potassium hydrogen difluoride[8], an effective means of decomposition for almost all resistant minerals occurring naturally in coals. The procedure involved filtering the sample through a 7cm diameter Whatman 42 filter paper which was ashed in a platinum crucible. 0.2g of KHF_2 was added and the mixture was fused over a low heat. The product was decomposed in 1ml $HClO_4$ and evaporated to dryness. A further 0.5ml $HClO_4$ was added and the solution again taken to dryness before being dissolved in 5ml 4M HCl and diluted to 50 ml. This sub-sample was kept separate from the main filtrate solution.

Pulverized Fuel Ash. Pulverized fuel ash was dissolved by fusing with a lithium metaborate/lithium tetraborate (80:20) flux (Johnson Matthey Spectroflux 100B) following the method of Thompson and Walsh[9]. This fusion method is advantageous in requiring a relatively low flux:sample ratio. A ratio of 3:1 (1.5g flux, 0.5g sample) proved optimal for the decomposition of pulverized fuel ash. The fusion product was dissolved in 100ml

of 0.4M HCl. The fusion is effective for not only important REE-bearing minerals that might be inherited from the coal, but also highly resistant spinels that form in abundance in some pulverized fuel ashes during coal burning.

Bulk REE Separation

Prior to ion chromatographic analysis, it is necessary to remove the bulk of the matrix, as this includes large amounts of transition metals that would otherwise overload the analytical column. The matrix was separated by cation exchange using a 2 x 19 cm column of strong acid cation exchange resin (Spectra/Gel 100-200 mesh 50X8 H^+ form). The method is essentially similar to that of Strelow and Jackson[10] which has been widely applied to sample preparation for REE analysis by ICP-AES[10][11]. The sample (0.4M HCl) was loaded onto the column and the matrix elements eluted with 550ml 1.75M HCl. The REE fraction was collected in 550 ml 4M HCl, which was evaporated on a hot-plate to <2ml and made up to 20ml with distilled water in a volumetric flask. The final acid concentration approximated 0.5M, and 20ml is sufficient to allow at least four replicate analyses of low ash coal. Where a "mini-fusion" had been necessary, the resulting solution was loaded onto the column before the main solution.

Ion Chromatographic Analysis

REE analysis was performed on a DIONEX 4000i gradient ion chromatograph, manufactured by the Dionex Corporation, Sunnyvale, California, using a CS-5 separator column and CG-5 guard column from the same manufacturer. The REE exist as trivalent cations in the sample solution. The very similar ionic properties of the REE preclude separation of the individual elements as trivalent cations. An increase in the selectivity of the ions is brought about by chelation with oxalic and diglycolic acid eluents. The REE are separated as oxalate and diglycolate anionic complexes with increased differential

charges[12]. The best practical separation of all the elements is achieved by using opposing linear gradients of the two chelating acid eluents.

Full analytical conditions are given elsewhere [12][13]. The Lu peak is inadequately resolved from that of Yb under these conditions (Fig. 1). However, the small Lu peak follows the larger Yb peak and does not contribute to its height, as measured from the chromatogram (Fig. 1) (see later). Ho cannot be determined by this method of analysis since the more abundant Y coelutes with Ho.

Although the sample matrix was removed by off-line ion exchange, it proved impossible to prepare REE sample solutions entirely devoid of trace (ppb) levels of transition metals, notably iron. These metals coelute with the REE under the conditions used. The problem was overcome using an initial elution with pyridine-2,6-dicarboxylic acid (PDCA) within the analytical programme. The transition metals form stable monovalent and divalent anionic complexes with PDCA and are removed as a group from the CS-5 separator column, whereas the REE form stable trivalent complexes with PDCA and are strongly retained on the column. Complete removal of the transition metals during the initial elution ensures a REE chromatogram free of interference from matrix elements.

The REE complexes were detected photometrically after post-column reaction with the metal complexing agent 4-(2-pyridylazo) resorcinol (PAR). A DIONEX UV/VIS variable wavelength detector was used at a wavelength of 520 nm. Data were collected by means of an IBM-compatible personal computer. Peak heights were measured using DAPA software (DAPA Scientific, Kalamunda, Western Australia). A single analytical run took 40 minutes with a further 12 minutes required for re-equilibration prior to the injection of the next solution.

South African pulverized fuel ashes generally contain concentrations of REE equal to, or greater than, those present in natural rocks. Accordingly, determination of the REE is possible by direct injection of the sample solution via a sample loop of between 50-200µl. High ash coals, such as SARM-20 (35% ash), can be injected similarly. However, coals of low ash content have insufficient REE to allow satisfactory analysis by direct injection,

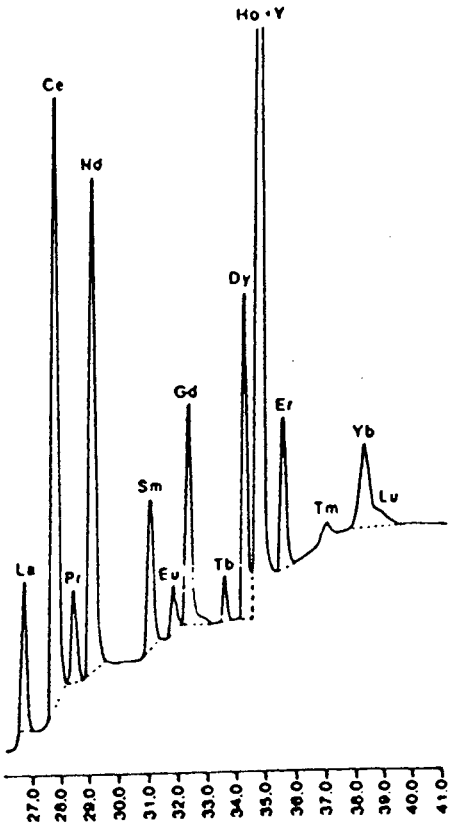

Fig. 1: REE chromatogram from analysis of a sample of USGS CLB-1 (see Table 3 for element concentrations). "Peak height" was recorded along a vertical line from peak apex to the selected baseline (dashed line). Note the inadequate resolution of Lu, and the rise in baseline which results from the use of an eluent gradient.

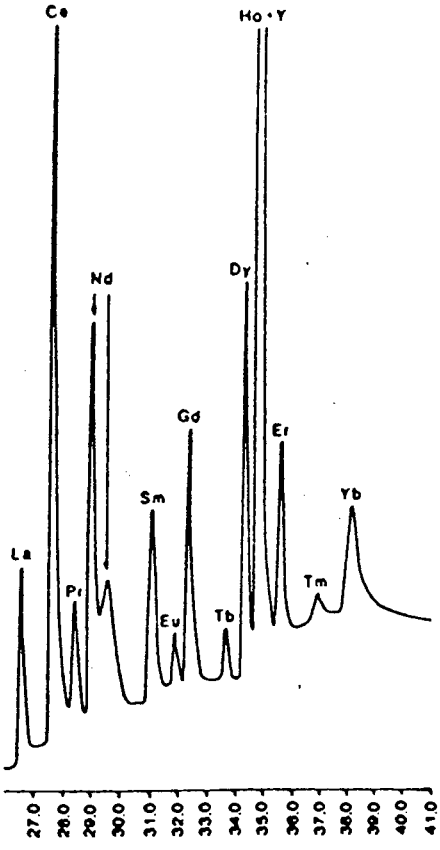

Fig. 2: Inferior REE chromatogram of a sample of USGS CLB-1 showing the splitting of the Nd peak resulting from an impurity in the PDCA eluent. The analytical programme used in this case results in the contraction of the last part of the chromatogram (cf. Fig. 1), thus increasing the peak heights for Er, Tm and Yb.

given the small sample size of 0.2g. In order to analyse low ash, low REE coals, on-line sample concentration was employed. In this additional step, an auxiliary pump was used to pump the sample solution onto a small "concentrator column", REE from the sample volume, typically 3-5ml, being retained on this column. This small column was then

switched into the eluent path, so transferring the REE to the separator column. Since the sample concentration could be performed while the system was re-equilibrating after the previous analysis, there was no addition to the time required for analysis.

Similar on-line concentration has previously been employed in ultra-trace element analysis of water[14] where the sample and standard were pumped onto the concentrator column at a pre-determined flow rate for an accurately measured period of time. This procedure gave very poor results when applied to the dissolved coal samples. Small differences in the HCl concentration of samples produced differing degrees of swelling on the concentrator column resin, thereby affecting the flow rate through the column. The difficulty was overcome by pumping a suitable volume of sample, dependent on the REE concentration, through the concentrator column, the volume of sample exiting the column being measured by means of a plastic, non-wetting, measuring cylinder.

STANDARDISATION AND SAMPLE ANALYSIS

REE concentrations were determined against a mixed REE standard solution prepared from commercially available 1000 ppm AAS single element standard solutions (Aldrich Chemical Co., Milwaukee; C.S.I.R., Pretoria). Concentrations of individual elements in the stock standard solution were designed to be equivalent to half of those that would be present in a preparation of a North American Shale Composite (NASC)[15]. Each standard solution was made up in 0.5M HCl to match the acid concentration of the sample solutions. Samples and/or the stock standard solution were diluted to provide a reasonable coincidence of REE levels.

The techniques described in this paper were tested by the repeated analysis of the international coal reference materials NBS-1632a and SARM-18 and fly ash reference materials NBS-2689, NBS-2690 and NBS-2691. Analyses of SARM-19 and SARM-20 were performed, both on samples prepared using microwave digestion and on ashed samples, to test the applicability of the microwave digestion and HPIC analytical techniques

to high ash coals. Results, included here, of a programme to determine the REE content of USGS CLB-1 are given in more detail elsewhere[3].

5 separate preparations were made each of NBS-1632a, SARM-18 and CLB-1 and each preparation was analysed in duplicate. Only on the rare occasion that the duplication was worse than 10%, indicating a malfunction in the analytical procedure, was a third analysis undertaken.

A standard solution was run after each sample, in the case of NBS-1632a, SARM-18 and USGS CLB-1, or after every second sample. Considerable care was taken in the determination of peak intensities from the REE chromatograms for samples and standards (Fig. 1), with base-lines precisely defined for each peak. Element concentrations were calculated by comparison of the heights of sample and standard peaks, "peak height" providing a more accurate means of analysis than "peak area".

RESULTS

Precision

In an earlier study on silicate rocks, le Roex and Watkins[1] found instrument precision to be better than 5% CoV for all REE (Tm was not reported). Accuracy of the results from this earlier study could be gauged from the close comparison of results with published data from other analytical techniques[1]. Sources of imprecision in the analytical technique applied to coals and pulverized fuel ashes originate from (i) the different methods of sample preparation, and (ii), in the case of the low ash coals, use of the novel means of on-line sample concentration.

The precision of the on-line sample concentration procedure was tested by analysing a single solution of NBS-1632a five times in sequence. The results showed a CoV of better than 4% for most elements, with only Eu (5.7%) and Tm (11.0%) showing greater relative error on account of their low concentration in the sample. The reproducibility associated

with the entire procedure of coal analysis is indicated by the standard deviation and CoV of results from the multiple analysis of the low ash coals (Tables 1 - 3). Precision for each element was generally <5% CoV, in spite of the small (0.2g) sample size. Significantly poorer precision was obtained for Tm in the analysis of CLB-1 since the concentration of this element was close to the lower limit of detection. The small Tm peak was measured by "peak area". Enhanced reproducibility for Tm can readily be achieved by greater on-line sample concentration. This, however, was not routinely undertaken in this study, as it would have rapidly exhausted the sample solutions, so preventing repeated analysis of individual samples. A poorer than usual precision recorded in the analysis of CLB-1 for a number of the REE can be explained by heterogeneity in the distribution of trace REE-bearing minerals in the powdered sample and the consequent increase in sampling error due to the small 0.2g sample size[3].

Results from the analysis of the 3 fly ash standard reference materials are given in Table 4. In each case satisfactory REE determination was achieved by direct injection of the sample solution using a 100 µl sample loop. As with the coal analyses, however, Tm was present either below or only slightly above the limit of detection, and is not reported.

Accuracy

Assessing the accuracy of the results from the present study is made difficult by the paucity of available REE data for the reference materials, particularly the fly ashes. The results of HPIC analysis for NBS-1632a, SARM-18 and CLB-1 are compared to those obtained by INAA and available reference values[16][17] in Tables 1 - 3 . The results for USGS CLB-1 are generally closely comparable to the means of values obtained from other laboratories using alternative techniques of REE analysis (J. Kane *pers. comm.*) (Table 3). The generally smooth plots obtained when the REE concentrations from HPIC analysis are normalised to chondrite values (Fig. 3) provides some confidence in the quality of data.

Table 1: REE concentrations (in ppm) for NBS-1632a by HPIC analysis compared to results from INAA and published data.

NBS-1632a (n=3)						
	HPIC			INAA	NBS(1984)	
	$\bar{x}$	sd	%CoV		$\bar{x}$	sd
La	12.4	0.40	3.19	15	15	3
Ce	25.7	0.22	0.85	31	29	2
Pr	3.17	0.05	1.55	2.9	3.2	-
Nd	11.1	0.30	2.75	14	11.4	1.3
Sm	2.24	0.07	3.01	2.60	2.4	0.3
Eu	0.46	0.01	3.10	0.51	0.527	0.023
Gd	1.92	0.04	1.98	-	2.4	0.5
Tb	0.29	0.01	2.98	0.35	0.31	0.02
Dy	1.76	0.01	0.40	1.9	2.1	0.2
Er	1.00	0.02	1.76	1.1	0.91	-
Tm	0.16	0.01	4.43	-	0.40	-
Yb	0.94	0.002	0.25	1.1	1.03	0.12

Table 2: REE concentrations (in ppm) for SARM-18 by HPIC analysis compared to INAA and published data.

SARM-18 (n=4)							
	HPIC				INAA	Ring & Hansen (1984)	
	MICROWAVE			ASHED			
	$\bar{x}$	sd	%CoV			$\bar{x}$	Range
La	8.79	0.23	2.64	8.33	9.2	10	9 - 13
Ce	19.1	0.32	1.66	18.2	21.8	22	21 - 24
Pr	2.32	0.04	1.75	2.10	2.6	-	-
Nd	8.49	0.10	1.15	8.17	11	-	-
Sm	1.61	0.09	5.51	1.64	1.9	2	1.9 - 2.2
Eu	0.31	0.004	1.21	0.28	0.31	(0.3)	-
Gd	1.55	0.04	2.33	1.59	2.0	-	-
Tb	0.26	0.004	1.36	0.27	0.32	(0.3)	-
Dy	1.73	0.03	1.76	1.72	2.03	-	-
Er	1.15	0.02	1.67	1.14	1.29	-	-
Tm	0.19	0.01	3.11	-	0.2	-	-
Yb	1.10	0.02	2.07	1.12	1.26	-	-

Table 3: REE concentrations (in ppm) for USGS CLB-1 by HPIC analysis.

USGS CLB-1 (n=3)						
	HPIC			J.S. Kane *(pers.comm.)*		
	$\bar{x}$	sd	%CoV	$\bar{x}$	n	Range
La	5.38	0.24	4.43	5.28	11	2.70 - 6.22
Ce	11.0	0.36	3.30	11.51	12	8.48 - 19.44
Pr	1.39	0.04	3.04	0.97	2	0.58 - 1.36
Nd	4.91	0.08	1.62	5.12	8	3.87 - 5.89
Sm	1.00	0.04	4.32	0.99	6	0.34 - 1.25
Eu	0.24	0.03	12.31	0.24	7	0.22 - 0.26
Gd	0.97	0.03	3.38	1.07	2	1.02 - 1.13
Tb	0.16	0.01	3.37	0.16	7	0.14 - 0.20
Dy	0.94	0.03	2.71	0.96	1	-
Er	0.57	0.03	4.40	0.55	1	-
Tm	0.09	0.003	3.71	0.08	2	0.08 - 0.09
Yb	0.49	0.02	4.89	0.53	9	0.41 - 0.74

Table 4: REE concentrations (in ppm) by HPIC analysis of fly ashes NBS-2689, NBS-2690 and NBS-2691.

	NBS-2689	NBS-2690	NBS-2691
La	77.9	64.9	58.6
Ce	145	112	107
Pr	17.3	13.2	12.7
Nd	66.8	47.6	47.5
Sm	13.6	9.29	10.1
Eu	2.69	1.96	2.18
Gd	12.6	8.38	9.20
Tb	2.02	1.27	1.44
Dy	12.4	8.03	8.78
Er	7.35	4.90	5.12
Yb	6.82	4.65	4.73

Where high ash coal reference materials SARM-19 and SARM-20 were analysed after ashing there is a small but significant reduction in the concentrations of the light REE compared to those obtained after microwave dissolution (Tables 5 - 6). The dissolution procedure used for coal ash was the same as that applied to pulverized fuel ash samples.

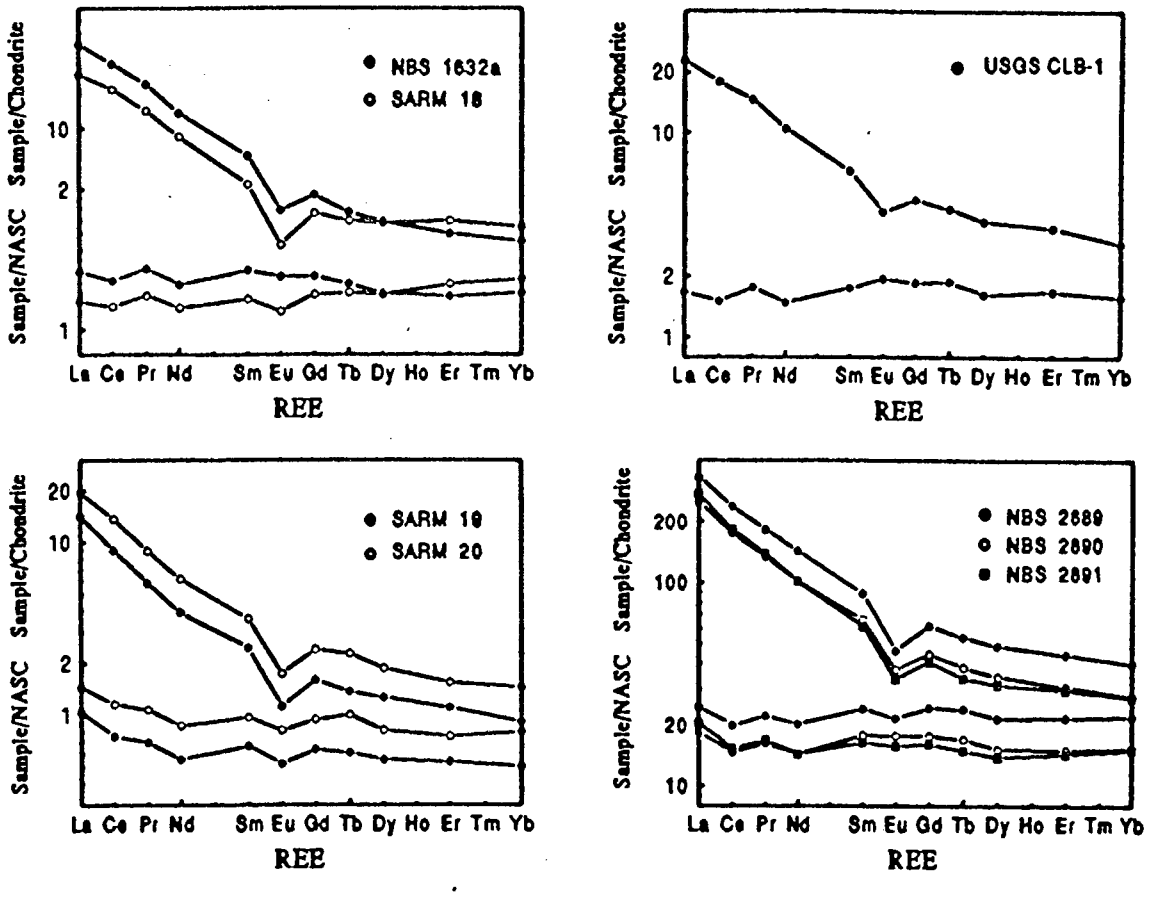

Fig. 3: REE abundances in coal and pulverized fuel ash CRMs normalised to chondrite[19] and North American Shale Composite[15] values.

Limits of Detection

Lower limits of detection will naturally vary according to the size of sample loop and the degree of sample preconcentration employed in the analysis, and will be different

Table 5: REE concentrations (in ppm) for SARM-19 by HPIC analysis after microwave dissolution and preparation by ashing compared to INAA and published data.

SARM-19				
	HPIC		INAA	Ring & Hansen (1984)
	MICROWAVE	ASHED		
La	33.4	22.4	25.8	27
Ce	55.0	46.6	56.4	56
Pr	5.50	4.85	6.7	-
Nd	18.4	18.3	26.4	-
Sm	3.75	3.48	4.49	4.9
Eu	0.65	0.63	0.70	(0.7)
Gd	3.27	3.20	4.3	-
Tb	0.51	0.53	0.65	(0.7)
Dy	3.20	3.20	3.62	-
Er	1.82	1.86	2.4	-
Tm	-	-	-	-
Yb	1.56	1.76	1.93	(2)

Table 6: REE concentrations (in ppm) for SARM-20 by HPIC analysis after microwave dissolution and preparation by ashing compared to INAA and published data.

SARM-20				
	HPIC		INAA	Ring & Hansen (1984)
	MICROWAVE	ASHED		
La	46.3	37.7	43.6	43
Ce	83.8	73.4	87.8	87
Pr	8.49	7.74	8.5	-
Nd	28.7	28.1	33.6	-
Sm	5.49	5.24	6.22	6.3
Eu	1.01	0.88	1.02	1
Gd	4.90	4.60	4.5	-
Tb	0.85	0.78	0.91	(0.9)
Dy	4.74	4.69	4.80	-
Er	2.56	2.58	2.7	-
Tm	-	-	-	-
Yb	2.47	2.32	2.67	(2)

for each element. With the sample sizes and procedures used in this study, the limits of detection were in the order of 10ppb in the original coal or pulverized fuel ash.

DISCUSSION OF TECHNIQUE

Modern HPIC is a highly flexible analytical technique. The changing of various parameters in the analytical methodology, notably eluent and post-column reagent composition, eluent gradients, and the wavelength of detection, can be used to modify subtly the REE chromatogram. Changes in eluent composition, in particular, can have profound effects on the chromatogram, leading to significant problems when such changes occur inadvertently. In addition, alternative separation chemistry can afford significantly different analytical capabilities. While it is impossible in this paper to discuss all of the many factors affecting REE analysis by HPIC, there follows a discussion of some of the more important factors considered in the development of our present technique for routine application to coals and pulverized fuel ash.

Sample Size

REE are contained in coals almost exclusively in the inorganic "ash" component, which comprises typically 3-50 percent of the coal. Within this inorganic fraction the REE may be highly concentrated in individual REE-bearing minerals, such as zircon and apatite. The REE may be liberated into the glass of pulverized fuel ash, although the highly refractory zircon is liable to persist as a REE host. For this reason, fine crushing and homogenisation of the coal and pulverized fuel ash samples is essential. Even if this is achieved, it remains highly desirable for representative analysis to use as much sample as possible. The use of 0.2g of coal in the present study is considered to be too small a sample. 0.5g is a more realistic sample size to ensure representative sampling of a low ash

coal such as USGS CLB-1 which has an ash content of only 5.4 wt % (J. Kane *pers. comm.*). In future studies the use of higher pressure (120 bar) digestion vessels in the microwave oven should allow for dissolution of 0.25g sample aliquots, giving a 0.5g sample size when employing the present procedures.

There is little doubt also that modifications can be made to the off-line bulk separation of the REE, with savings in time and the quantity of acids used. However, where, as in our laboratory, a facility is designed for the successful analysis of a wide range of sample types with very different matrices, there is limited scope for refining the separation procedure specifically for coals.

Separation Chemistry

Alternate ion chromatographic methods using *cation* separation for the determination of REE in geological materials have been reported[12][16]. These employ a-hydroxyisobutyric acid (HIBA) as a chelating agent, which forms positively charged complexes with the REE. The REE of heaviest atomic mass, with smallest ionic radius, form the least positively charged complexes[12][13] and are eluted first from the cation separator column. Hence the elution order of the REE by *cation* separation is the reverse of that of the *anion* separation technique described here (Fig. 4).

A clear advantage of an elution sequence Lu - La is the ability easily to determine Lu, since its peak is fully resolved from that of Yb. The sharper peaks, typical of early eluting elements (Fig. 4), have the further advantage of providing good sensitivity in "peak height" for Lu and Tm, which are normally present in coals and pulverized fuel ashes in very low concentrations. The *cation* method also allows the determination of Ho, although Dy can no longer be determined owing to coelution with Y.

The Lu - La elution sequence can be disadvantageous in the determination of Eu. Eu is a critical element in geochemical studies since it alone amongst the REE may exist

in the divalent state in magmatic environments, and is consequently fractionated relative to the other REE during crystallization. Resulting Eu anomalies, both enrichment and depletion, yield important petrogenetic information. The abundance of Eu in rocks is

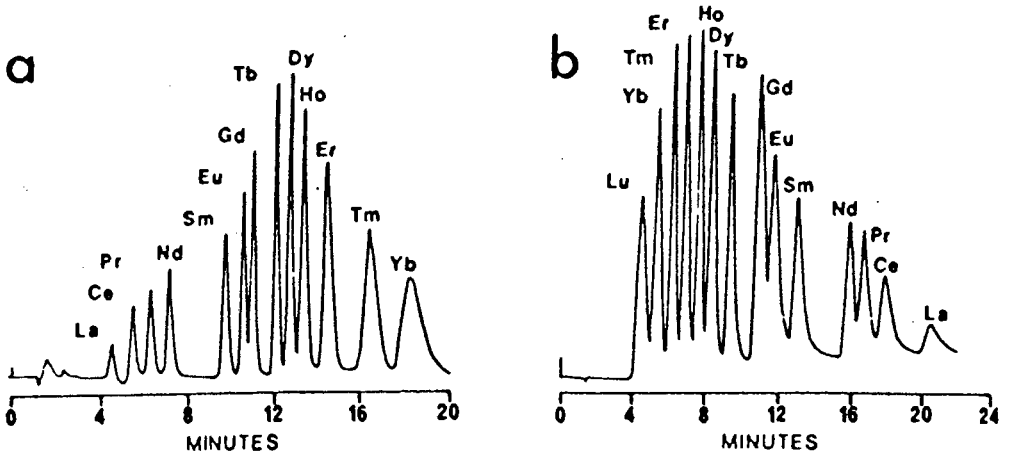

Fig. 4: Chromatograms produced for solutions containing equal concentrations of each REE by (a) anion separation and (b) cation separation, showing the relative sensitivity for each element when reacted with PAR. (after DIONEX[13]).

normally appreciably lower than that of the adjacent REE, Gd. The Eu and Gd peaks are closely spaced in the REE chromatogram, and since they lie in the middle portion of the chromatogram, it is difficult to effect greater separation by modification of eluent composition and gradients. When Eu elutes *before* Gd, as in the *anion* separation, it is normally possible to resolve fully the two peaks (Fig. 1). However, in the *cation* separation technique described by Heberling et al. [12], significant tailing of the much larger Gd peak onto the small Eu peak can be expected (Fig. 2), compromising the accuracy of the Eu determination. During *anion* separation, the Sm peak does not tail onto Eu as Sm elutes appreciably before Eu (Figs 1, 4a).

However, the fundamental reason for the choice of the *anion* separation method in

our laboratory was the ability to remove transitional metal contaminants in the sample solutions from the CS-5 column with PDCA eluent, thus avoiding peak overlap problems in the REE chromatogram. Attempts to remove trace transition metals during analysis by *cation* separation have so far been only partially successful.

Element Sensitivity

The relative sensitivity of visible light detection at 520 nm for each REE after complexing with PAR is illustrated in Fig. 4. Varying the wavelength of detection can slightly modify this pattern. The relative sensitivity shown in Fig. 4 is generally convenient for the analysis of REE in geological materials, including coals and pulverized fuel ash. Reduced sensitivity for the light REE (La - Sm) balances their greater concentrations in most geological samples. Tb, which is of very low abundance, lies in the area of maximum sensitivity and only for the heaviest REE, Er - Lu, is the sensitivity inappropriate.

The sensitivity of detection is affected significantly by the composition of the post-column colouring reagent. As an example, the addition of 1M Dimethylaminoethanol (DMEA) to the PAR post-column reagent increases the sensitivity ~10-fold for La and ~2-fold for Yb. Whilst being an appreciable advantage in detecting individual elements occurring in low concentration, the disparity between the responses for the light and heavy REE makes the routine addition of DMEA impractical in routine analysis. Its use in our laboratory is reserved for silicate rocks showing a relative depletion in the heavy REE. A less dramatic, but more universal, increase in sensitivity may be gained by the use of a heater on a post-column reaction coil.

Standardisation

It is clearly desirable to determine all of the REE in a single analytical run. This

is normally possible in the case of coals and pulverized fuel ash which do not exhibit highly fractionated REE patterns, although the concentration of Tm is usually too low for accurate determination. It is preferable to match adequately the standard concentrations to those of the sample solution. In the present study simple dilution of the stock standard solution, reflecting the relative REE concentrations in the NASC[15], provided suitable standards for coal and pulverized fuel ash analysis. The calibration line using "peak height" is straight for each REE. However, in samples with highly fractionated REE patterns and/or severe Eu depletion, as commonly is the case for granitic rocks, it may prove necessary to analyse the sample in two runs having different dilutions, since the separator column is of low capacity and can become saturated. This may occur when using a 100 µl injection loop in rock solutions where Ce, the most abundant REE, is >~4 ppm in the solution. Column saturation giving rise to non-linear calibration is usually readily detected by the poor shape of chromatographic peaks and a reduction in retention times.

Eluent Chemistry

Chemical behaviour within the REE analyses can be complex, with small variations in eluent chemistry having dramatic, often catastrophic, results on the chromatogram produced. Consequently, very great care is required in preparing the eluents. Extremely low concentrations of transition metals are required in the water used for rinsing of the separator column during the analytical programme to avoid their build up on the column and subsequent coelution with the REE. The running of a sample blank after any eluent change is a wise precaution to avoid systematic errors arising from interfering peaks on the chromatogram.

All chemicals used in the HPIC analysis were of analytical grade. Even so, experience has shown that changing from one brand of chemical to another of equal specification can give rise to important changes in the REE chromatogram. The dangers of minor variations in eluent chemistry are well illustrated by a problem that bedeviled the

HPIC REE analysis in our laboratory, and was solved and corrected only after completion of this study. After the CS-5 separator column had been used for a number of analyses, deterioration of the shape of the Nd peak was observed. This started as a broadening of the base of the peak, but developed into a definite shoulder and eventually into a second, poorly resolved peak (Fig.2). No interference was visible in the blank, and investigations indicated the cause to be a two-fold elution of Nd, which presumably was forming two different complexes during the analysis. The problem necessitated frequent replacement of the CS-5 columns, considerably increasing the cost of analysis. The problem was finally resolved by the use of a highly refined PDCA, manufactured by Dionex Corporation, suggesting that an unidentified contaminant in the various other PDCA brands used was responsible. In order to minimise the problem of disturbance to the REE chromatograms, both eluents and the post-column reagent should be made up extremely precisely. While the highly accurate weighing of chemicals is unnecessary for satisfactory analysis, it does allow the continuous close monitoring of instrument performance.

The laboratory is air conditioned to 20°C. A stable ambient temperature is preferable for analysis at ultra trace levels. Each of the eluents employed in the HPIC analysis has shown no significant deterioration after preparation during their period of use in the laboratory, which has been as long as 2 months. The oxalic acid and PDCA eluents are prepared in 21 volumes, so minimising the frequency of change over. The diglycolic acid eluent is prepared in smaller 11 volumes on account of its much smaller consumption. As far as possible, only a single eluent is changed on any occasion, so as to facilitate the tracing of problems arising from variation in eluent composition. Eluents are deoxygenated by sparging with He before use.

The PAR post-column reagent is prone to oxidation, resulting in sedimentation. PAR is prepared in 21 volumes, with 11 being stored in a refrigerator. The 21 allows ~50 hours of analysis between preparations. The PAR has been found to be stable over a period of 2 weeks in our laboratory. Alternative metal colouring agents, such as arsenazo-III, whilst having some possible advantage in sensitivity, may be prone to more rapid

decomposition.

Gradients

The ability of the DIONEX 4000i instrument to run gradients involving up to 4 eluents enables satisfactory resolution of the REE peaks, not possible with elution by an eluent of constant composition - "isocratic elution". Minor changes to the gradient programme can pay dividends in the quality of the chromatogram, although development work in this field is extremely time-consuming. Improvement in the resolution or sensitivity in one part of the chromatogram frequently gives a poorer result elsewhere, and there is inevitably a trade-off between the degree of resolution and the breadth/sensitivity of the peaks.

For routine analysis, frequent adjustment to the gradient programme is impractical and compromise programmes giving satisfactory peak heights and resolution for a range of compositions are required. In our laboratory, two gradient programmes are utilised in the routine analysis of rocks, including coals and pulverized fuel ashes. These differ only slightly in the proportions of the opposing oxalic acid/diglycolic acid used to remove the REE from the CS-5 separator column. The chromatogram shown in Fig. 1 was produced using the usual gradient programme[1][12][13]. The second programme is employed when concentrations of the heaviest REE are low. Its use affects only the last part of the chromatogram which is condensed, narrowing the Er, Tm and Yb peaks and so increasing their sensitivity. The wide separation of Er, Tm and Yb peaks is reduced but the peaks remain adequately resolved. This programme is not suitable for samples in which the heavy REE are more abundant, as the condensing of the chromatogram results in tailing of the larger Er peak onto that of Tm. The condensing of the chromatogram also causes a steepening of the slope of the baseline which can make accurate measurement of peak heights more difficult. Further modification of the gradient programme may provide sufficient resolution of the Yb and Lu peaks although precise Lu values are better provided

by the alternative cation separation technique mentioned previously.

Despite the essential advantages yielded by gradient elution, it does add further complexity to the analytical chemistry. An obvious result is the fluctuation in baseline on the chromatogram (Fig. 1). The geometry of the baseline is usually not a problem for actual REE determination, although it may call for specific procedures of peak measurement. Particular care is required when changing eluents or replacing the separator column to make sure the chromatogram is free of spurious background peaks that may adversely affect the results, and once more it is prudent to run a sample blank at this time. Otherwise, monitoring of the peak heights of regularly run standards will normally indicate the presence of an interference on the chromatogram.

Peak Measurement

In many HPIC applications using isocratic elution, well-resolved peaks lie on a flat baseline. Chromatograms of this type are readily integrated with high precision using automated software packages. Typically "peak area" is used with the peaks simply defined by the inflexion points from the baseline. The chromatograms produced in REE analysis present a different situation. The DAPA software package, used in processing the REE chromatograms, allowed the setting up of a peak height estimation programme that treated individual peaks in specific ways. However, small variations in the retention times of individual elements required that each chromatogram was checked for correct peak height estimation. In this way, routine but not automatic analyses were possible.

The resolution of the REE peaks in most cases is sufficient to allow the use of baselines drawn from start to end of peaks (Fig 1.). The large size of the peak given by the coelution of Y with Ho requires that a baseline be specifically defined for the preceding Dy peak. A similar procedure may be required for the Eu peak. Care must also be taken in the consistent estimation of the Yb peak owing to the following unresolved Lu peak. The use of "peak height" has proved to be more accurate and precise than "peak area", due

to the reduction in the degree of interference between adjacent peaks. Consideration of the typical shape of the chromatographic peaks is required in formulating the peak height estimation programme, with use being made of the fact that the peaks "tail" only onto following peaks, not onto preceding peaks.

CONCLUSIONS

HPIC provides a useful addition to the available techniques for determining the concentrations of REE in geological materials. The method used in this study has proved satisfactory for the production of high quality REE data for coals and pulverized fuel ashes. Limits of detection and precision of the analyses are at least comparable to INAA and ICP-AES, the most widely available alternative techniques. The ability of the present technique to determine 12 of the REE, including all of the petrogenetically important elements, is advantageous.

Microwave digestion has proved to be a practical means of dissolving coals. Up to 8 pressure vessels may be irradiated simultaneously affording considerable time savings in sample preparation without risk of contamination. The use of higher pressure digestion vessels than were available for the present study should ensure a satisfactorily representative sample size.

A particular advantage of the HPIC technique would appear to lie in the low cost of instrumentation (<$50,000) and individual analyses ($20 per duplicate for *consumables*, including separator column replacement). With its further advantage over INAA of rapidity of analysis, and the clear disadvantage of the latter technique in requiring access to a nuclear reactor, HPIC would appear to have greater potential for expansion of future REE analytical facilities.

The flexibility of the technique allows for fine tuning to particular needs. The very small volume of sample solution required for an analysis and the ability to concentrate the

sample solution on-line makes HPIC suitable for the analysis of coals of low ash content, as well as for high ash coals and pulverized fuel ash.

Whilst the choice of an analytical instrument is likely to be influenced by extraneous factors, such as the available expertise and equipment already in place, HPIC would appear to be particularly attractive in newly established facilities, on account of the low capital and maintenance costs of the equipment.

The complex chemistry involved in determining REE in geological materials by HPIC demands that the analytical facility is supervised by an analyst with some chemical training. Chemical expertise is certainly required if the technique is to be optimised for application to a particular sample type, such as coal and pulverized fuel ash.

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